

## Final report: IRI Project: contract no. F61775-02-C4029, June 2002-May 2005

The broad objectives of this IRI project which ran during three years, June 2002- May 2005, were the investigations of the spectroscopic properties of boron species, their aggregation and reactions in matrices ranging from neon to those doped with hydrogen. The studies of the aggregation properties were hampered by the lack of spectroscopic knowledge on the electronic transitions of the polyatomic boron molecules and their ions. Thus it was clear that their identification at first had to be undertaken in order to proceed on this. The same applies to reactions in hydrogen doped matrices. This was accomplished for  $B_3$  and  $B_3^-$ . In addition theoretical predictions for the future studies of the  $B_4$  species and its positive and negative ions were completed. The project was initially instigated on the advice and recommendation of Dr.C.W.Larson, AFRL, Edwards Air Force Base, California, whose continual guidance, suggestions and enthusiasm throughout the project were much appreciated.

For the purpose of the spectral identification and characterisation of polyatomic boron molecules, a world-wide unique apparatus, combining mass-selection (using a cesium sputter source) with a matrix isolation technique was initially used, backed up by theoretical calculations. The six, 6-month interim reports summarized the experiments undertaken, including the unsuccessful ones. Because the electronic spectra of the triatomic boron species were identified in 5 K neon matrices, an ambitious project to observe the gas phase spectrum of  $B_3$  could also be realized.

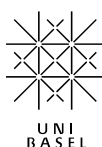
The project as a whole proved rather successful and productive as evidenced by 5 publications during this three year period in leading journals of chemical physics:

“Electronic absorption spectra of  $B_3$  and  $B_3^-$  in neon matrices and ab initio analysis of the vibronic structure”

M.Wyss, E.Riaplov, A.Batalov, J.P.Maier, T.Weber, W.Meyer and P.Rosmus  
Journal of Chemical Physics, **119**, 9703, 2003.

“Gas phase detection of cyclic  $B_3$ :  $^2E' - X^2A_1'$  electronic origin band“

P.Cias, M.Araki, A.Denisov and J.P.Maier  
Journal of Chemical Physics, **121**, 6776, 2004.



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“The near infrared  $1^2 A_2'' - X^2 A_1'$  electronic transition of  $B_3$  in a neon matrix”

A.Batalov, J.Fulara, I.Shnitko and J.P.Maier

Chemical Physics Letters, **404**, 315, 2005.

“Vibrations in the  $B_4$  rhombic structure”

R. Linguerri, I.Navizet, P.Rosmus, S.Carter and J.P.Maier

Journal of Chemical Physics, **122**, 34301, 2005.

“Theoretical study of the electronic excited states of  $B_4$ ,  $B_4^+$  and  $B_4^-$ ”

C.Gillery, R.Linguerri, P.Rosmus and J.P.Maier

Z. Phys.Chem., **219**, 467, 2005.

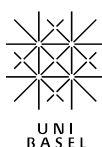
These five publications summarize the results and success of this IRI project and are included with this report.

The project involved experimental studies using our special matrix apparatus in Basel with which a number of PhD students worked during this period, starting with M.Wyss, E.Riaplov (both PhD now) and continued by A.Batalov, I.Shnitko. They were assisted in the experiments by the annual visits of Dr.J.Fulara, a long standing collaborator from the Polish Academy of Sciences, Warsaw, and succeeded in the measurement of the electronic spectra of  $B_3$  and  $B_3^-$  in neon matrices. As a follow up to this the gas phase spectrum of  $B_3$  was obtained by the students P.Cias (now PhD), A.Denisov, working under the guidance of Dr.M.Araki.

The interpretation of the vibronic structure and symmetry of the electronic transitions of  $B_3$  and  $B_3^-$  proved possible as result of extensive collaborations with two theoretical groups: that of Prof.P.Rosmus, University of Marne la Vallee, France and Prof.W.Meyer, University of Kaiserslautern, Germany. P.Rosmus spent 1-2 month periods in each of the three years of this IRI project as a guest Professor here working on the structure and spectroscopy of boron species, predicting their geometric, electronic and vibrational patterns. Two of his PhD students (C.Gillery, R.Linguerri) also had sojourns in Basel and these theoretical studies are a major part of their theses.

Though the IRI project has come to an end, we plan to continue our spectroscopic studies of the boron clusters. Specifically the tetraatomic and larger boron molecules could be studied in the gas phase by multiphoton ionisation and laser induced fluorescence methods- the instrumentation for which is available in our laboratory in Basel- combined with a laser ablation source. For the neon matrix experiments a new ion source, incorporating a high repetition laser vaporization design, for the deposition of the larger boron ions is in construction.

EOARD is thanked gratefully for providing this three year contract which has enabled us to open up a new area of research for boron clusters, led to multi-national collaborations and resulted in interactions and possible projects for the future with several groups in the U.S.A. on such and related research.



“The Contractor, Professor John P.MAIER, hereby declares that, to the best of his knowledge and belief, the technical data delivered herewith under contract No. F61775-02-C42029 is complete, accurate and complies with all the requirements of the contract”

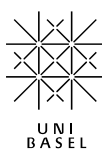
Date: Basel 26. June 2005

Name and Title of Authorized Official: Professor John P.Maier

“I certify that there were no subject inventions to declare as defined in FAR 52.227-13, during the performance of this contract”

Date: Basel 26. June 2005

Name and Title of Authorized Official: Professor John P.Maier



# Electronic absorption spectra of $B_3$ and $B_3^-$ in neon matrices and *ab initio* analysis of the vibronic structure

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Mass selected  $B_3^-$  ions have been isolated in 6 K neon matrices and their absorption spectra measured. A band system with origin at 467 nm is assigned as the  $1^2E' \leftarrow X^1A'_1$  electronic transition of the cyclic anion. After photobleaching, the  $1^2E' \leftarrow X^2A'_1$  and  $2^2E' \leftarrow X^2A'_1$  band systems of neutral cyclic  $B_3$  are observed which start around 736 and 458 nm, respectively. Large scale *ab initio* calculations have provided potential energy surfaces for a variational treatment of the vibrational motion. Calculated band origins leave no doubt about the electronic symmetry assignments. The complex vibrational structure in the  $1^2E'$  state, which is due to relatively strong Jahn–Teller distortions, appears to be closely reproduced by the calculated vibrational energies and intensities, if the first observed stronger line is identified with the first vibrationally excited state, placing the “true” band origin of the  $1^2E'$  state at 775 nm where no signal with significant strength is apparent. The  $2^2E'$  state undergoes only a relatively weak Jahn–Teller distortion and shows a short progression with an observed frequency of  $981(10) \text{ cm}^{-1}$  that compares favorably with the theoretical frequency of  $973 \text{ cm}^{-1}$ . The  $1^2E'$  system of  $B_3^-$  shows a Jahn–Teller activity comparable to that of the  $1^2E'$  state of  $B_3$ . © 2003 American Institute of Physics. [DOI: 10.1063/1.1613251]

## I. INTRODUCTION

There has been a growing interest in the structure and energetics of small boron and boron containing molecules because they have a variety of applications such as for the construction of high temperature semiconductor devices, as chemical insulators, and in the production of refractory materials and explosives.<sup>1</sup> However, there is little information on the spectroscopy of pure boron species in the literature. Only the boron dimer<sup>2</sup> and its anion<sup>3</sup> appear to be well characterized experimentally and theoretically.

Two experimental studies have been carried out for  $B_3$ , both in rare-gas matrices. One of these is an electron spin resonance (ESR) investigation that has confirmed the presence of three equivalent nuclei in the  $2^2A'_1$  ground state<sup>4</sup> and the other is an infrared spectroscopic study in which the degenerate mode ( $e'$ ) has been observed for both  $^{11}B_3$  and  $^{10}B_3$  isotopomers ( $886$  and  $928 \text{ cm}^{-1}$ , respectively).<sup>5</sup> Several theoretical investigations on the  $B_3$  molecule have predicted an equilateral cyclic structure ( $D_{3h}$ ) with a  $2^2A'_1$  electronic symmetry,<sup>6–9</sup> and the vibrational frequencies in the electronic ground state. Of the low-lying excited electronic states, only the states of  $2^2A''_2$  and  $2^2E'$  symmetry are accessible from the  $2^2A'_1$  ground state by dipole allowed excitation. Several transition bands are expected in the near infrared and visible regions.<sup>7,8</sup> Because the Jahn–Teller distortion in the  $E$

states implies stretching of a strong bond, the  $B_3$  molecule should provide a very interesting example for vibrational motion that proceeds on two coupled surfaces even for the lowest vibrational quanta.

Data on the  $B_3^-$  anion are even more scarce. There is only a theoretical study predicting a linear  $1^1\Sigma_g^+$  electronic ground state for this species from MP4 calculations.<sup>9</sup> However, MR-CI calculations carried out as part of this work show clearly that the lowest energy isomer possesses a cyclic  $D_{3h}$  structure with a  $1^1A'_1$  electronic ground state. As far as larger negatively charged boron molecules are concerned, only the gas phase photoelectron spectrum of  $B_5^-$  has been reported.<sup>10</sup>

In the present work the electronic absorption spectra of  $B_3^-$  and  $B_3$  have been measured in neon matrices at 6 K following mass-selection. In order to provide symmetry assignments and an interpretation of the complex vibronic structure observed in the excited electronic state  $1^2E'$  of  $B_3$  as result of the Jahn–Teller effect, multireference configuration interaction (MR-CI) *ab initio* electronic structure calculations have been undertaken. Based on diabatic potential energy surfaces in analytical form, the vibrational motion has been analyzed in variational calculations using hyperspherical coordinates. For the lower transition of  $B_3$ , line intensities and a tentative vibronic assignment are presented.

## II. EXPERIMENT

The apparatus employed has been described previously.<sup>11</sup> The  $B_3^-$  anions were produced in a cesium sput-

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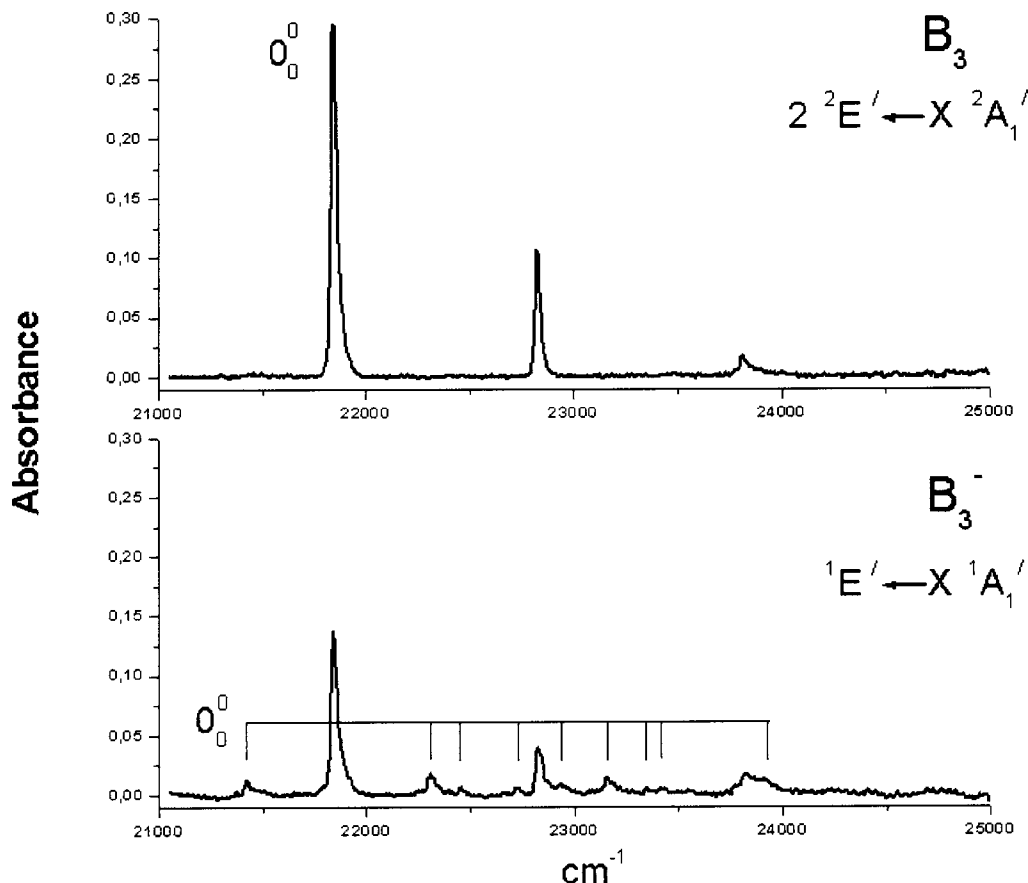


FIG. 1. Electronic absorption spectra recorded in a 6 K matrix after 4 hours of mass-selected codeposition of  $B_3^-$  with neon. The bottom trace shows the  $1^1E' - X^1A_1'$  electronic transition of  $B_3^-$  overlapped by the  $2^2E' - X^2A_1'$  system of  $B_3$ , produced from partial neutralization of the anions impinging on the matrix during deposition. The top trace reveals the  $2^2E' - X^2A_1'$  electronic transition of  $B_3$  measured after exposure to UV radiation. Absorption belonging to the anion disappears.

ter ion source that had been built originally for the production of carbon anions.<sup>12</sup> A boron-carbide ( $B_4C$ ) rod or pressed pure boron powder were used as sputter targets. The ions produced in the source were guided by an electrostatic lens system into a quadrupole mass analyzer, where the  $B_3^-$  anions were selected and then codeposited with excess of neon onto a rhodium coated sapphire plate at a temperature of 6 K. Ion currents of 25 nA using the boron sputter target and 10 nA from  $B_4C$  could be obtained for the mass selected  $^{11}B_3^-$  anions with unity mass resolution. All the experiments but one were performed with the  $B_4C$  precursor because the available pure boron sample was brittle.

Matrices of about 150  $\mu m$  thickness were grown during 4 hours. Absorption measurements in the 220–1100 nm range were carried out by passing monochromatic light from a halogen or xenon arc lamp through the matrix employing a waveguide-like technique and achieving a path length of about 2 cm. A medium pressure mercury lamp ( $E \leq 5.4$  eV) was used to neutralize the trapped ions. After exposure to the UV radiation the spectra were recorded again.

### III. OBSERVATIONS

#### A. Absorption system

Three unknown systems built upon the apparent band origins at 458, 467, and 736 nm were observed after mass

selected (33 u) codeposition of  $B_3^-$  ions with neon. As is illustrated by Fig. 1, exposure of the matrix to 5.4 eV radiation resulted in the complete disappearance of the 467 nm system and the growth of the 458 nm one. In addition, a new system starting at 736 nm evolved (Fig. 2), exhibiting a rich vibrational structure and correlating in intensity with the 458 nm one. Thus one concludes that the carrier of the 467 nm system is the  $B_3^-$  anion, whereas the 458 and 736 nm band groups are due to the neutral  $B_3$  species. Because natural boron contains about 20 percent as its  $^{10}B$  isotope, it was reasonable to check whether or not some of these newly observed absorptions belong to the  $B_2C$  molecule or its ion. This molecule is also produced in the cesium sputter source from a  $B_4C$  rod and its  $^{10}B^{11}BC$  isotopomer has the same mass as  $B_3$  and is, therefore, deposited as well. Nevertheless, even after deposition of  $^{11}B_2C^-$  (34 u), the production of which is much higher than that of  $^{10}B^{11}BC^-$ , neither of the above described systems were seen while usage of a pure boron rod in the source led again to the detection of the three band systems of Figs. 1 and 2 with the same intensity ratios. This supports the assignment of the absorptions observed to the  $B_3$  molecule and its anion.

The equilateral triangle structure of the neutral molecule  $B_3$  in the ground electronic state of  $^2A_1'$  symmetry is well established.<sup>9</sup> Dipole transition moments of symmetry  $A_2''$

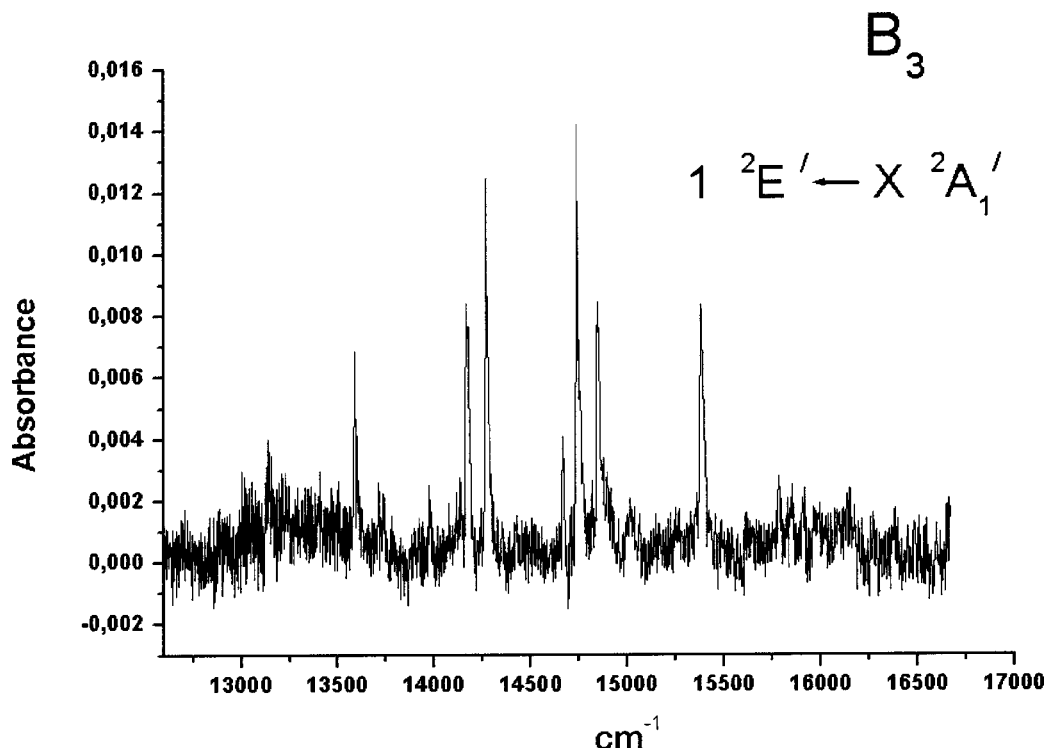


FIG. 2. Electronic absorption spectrum of the  $1\ ^2E' \leftarrow X\ ^2A_1'$  electronic transition of  $B_3$  recorded after 4 hours of mass-selected codeposition with neon followed by UV irradiation of the 6 K matrix.

$+E'$  connect this state only with states of symmetry  $^2A_2''$  and  $^2E'$ , respectively. As argued in detail later on, only  $^2E'$  states are available in the range of excitation energies investigated here.

Because the cyclic  $B_3$  neutrals are produced by photodetachment of the electron from the mass-selected  $B_3^-$  and isomerization of a linear to cyclic form of species held relatively rigidly in a 6 K neon lattice on irradiation with 3–5 eV photons is unlikely, the measured electronic spectrum of  $B_3^-$  is also ascribed to a cyclic isomer with ground state of  $^1A_1$  symmetry. This is in line with the observation that the excitation energy is close to the corresponding transition in neutral  $B_3$ , as to be expected from simple molecular orbital (MO) considerations since the same MOs are involved and the theoretical prediction for the transition (see Sec. IV). Therefore, the upper state of the band system observed is assigned to the  $^1E'$  electronic symmetry.

## B. Vibrational structure

The vibrational structure apparent in the observed electronic spectra (Figs. 1 and 2 and Tables I–III) is associated with excitation of the two normal modes,  $\nu_1(a_1')$ ,  $\nu_2(e')$ , in the upper electronic states because at 6 K the population is essentially all in the vibrationless level of the ground state. Because the upper electronic states of  $B_3$  and  $B_3^-$  have  $E'$  symmetry they are subject to Jahn–Teller distortions which may cause complex vibrational pattern.

The second system of  $B_3$ , assigned to the  $2\ ^2E' \leftarrow X\ ^2A_1'$  transition, has the simplest pattern: Starting with the origin band at 458 nm a seemingly regular progression mode is discernible (Fig. 1) with two spacings that are

the same within the error limit (Table III). As the origin band is dominant, no large geometry change is expected on passing from the ground to the excited electronic state.

In contrast, the vibronic structure of the first system of  $B_3$  (Fig. 1, top trace, Table II), assigned to the  $1\ ^2E' \leftarrow X\ ^2A_1'$  transition, indicates a strong Jahn–Teller distortion: The excitation of the degenerate  $\nu_2(e')$  Jahn–Teller active mode is evident. The two transition systems are not only very different in complexity, they also show quite different intensities: The spectra indicate an absorbance ratio of one order of magnitude in favor of the second band.

The absorption spectrum of  $B_3^-$  (Fig. 2, bottom trace, Table I), assigned to the  $1\ ^1E' \leftarrow X\ ^1A_1'$  transition, shows a complexity similar to the lower transition of  $B_3$ . The patterns of these two systems are really not simple and a sensible assignment can only be made by means of a theoretical treatment as attempted in Sec. V.

TABLE I. Positions of band maxima ( $\lambda \pm 0.2$  nm) observed in the  $1\ ^1E' \leftarrow X\ ^1A_1'$  absorption spectrum of  $B_3^-$  in a 6 K neon matrix

$\lambda$ (nm)	$\nu$ (cm $^{-1}$ )	$\Delta\nu$ (cm $^{-1}$ )
466.9	21 412	0
448.4	22 295	883
445.5	22 440	1028
440.2	22 711	1299
436.2	22 919	1507
431.9	23 147	1735
428.4	23 336	1924
427.1	23 407	1995
418.4	23 894	2482

TABLE II. Positions of band maxima ( $\lambda \pm 0.2$  nm) in the  $1^2E' - X^2A_1'$  absorption spectrum of  $B_3$ , vibronic symmetry  $\Gamma$  and calculated intensities.

$\lambda(\text{nm})$	$\nu(\text{cm}^{-1})$	$\Delta\nu(\text{cm}^{-1})$		$\Gamma$	Intensity
		Experiment <sup>a</sup>	Theory		
735.8	13 587	0	685	0	1.00
				230	
				685	1.45
				733	
715.5	13 972	385	1070	1074	0.74
				1073	
				1269	0.59
705.6	14 168	581	1266	1337	1.80
700.7	14 268	681	1366	1425	
				1660	
681.6	14 667	1080	1765	1732	0.25
				1818	1.70
678.3	14 739	1152	1837	1801	
				1910	
673.4	14 846	1259	1944	1933	0.60
				2123	0.20
				2195	
				2202	0.01
				2310	0.00
				2340	
				2384	
				2444	0.98
				2481	0.01
				2537	
650.0	15 380	1793	2478	2564	
				2648	
				2714	
				2728	0.03
				2762	
				2834	0.11
				2848	0.04
				2868	
				2915	
				2920	0.45
				3057	0.02

<sup>a</sup>For two different band origins, see text.

#### IV. THEORY

Symmetry assignments and analysis of complex vibrational structures as observed for  $B_3$  require the knowledge of sufficiently accurate and extended potential energy surfaces (PES) for low-lying electronic states. Because previous theoretical efforts have been limited to a few cuts through selected PESs,<sup>7</sup> we have performed large-scale *ab initio* calculations for the states relevant to the absorption spectra presented here.<sup>13</sup>

The orbital ordering for  $B_3$  in  $D_{3h}$  symmetry is  $1a_1'$ ,  $1e'$ ,  $2a_1'$ ,  $2e'$ ,  $1a_2''$ ,  $3a_1'$  for the orbitals occupied in the ground state, and  $3e'$ ,  $1e''$ ,  $4e'$ ,  $1a_2'$ , ... for the lower virtual orbitals. Clearly, the ground state is of  $^2A_1'$  symmetry and excited states accessible by dipole selection rules have  $^2A_2''$  and  $^2E'$  symmetries. While the  $1^2A_2''$  state is dominated by the single configuration resulting from the  $3a_1' \leftarrow 1a_2''$  excitation, two low-lying  $^2E'$  states should result from substantial mixing of the configurations corresponding to the excitations  $3e' \leftarrow 3a_1'$  and  $3a_1' \leftarrow 2e'$ , respectively. The ground state configuration of  $B_3^-$  is that of  $B_3$  but with an extra

TABLE III. Positions of band maxima ( $\lambda \pm 0.2$  nm) observed in the  $2^2E' - X^2A_1'$  absorption spectrum of  $B_3$ , calculated vibrational energies and vibronic symmetry  $\Gamma$ .

$\lambda(\text{nm})$	$\nu(\text{cm}^{-1})$	$\Delta\nu(\text{cm}^{-1})$		
		Expt.	Theory	$\Gamma$
458.0	21828	0	0	$E'$
			848	$A_2'$
438.3	22809	981	973	$E'$
			974	$A_1'$
			1258	$E'$
			1746	$E'$
420.1	23797	1969	1815	$A_2'$
			1951	$E'$
			2018	$A_1'$
			2144	$E'$

electron in the highest occupied orbital  $3a_1$ . The lowest dipole allowed excitation is here dominated by the  $3e' \leftarrow 3a_1'$  promotion.

A configuration mixing as indicated above, on top of the interaction between the two components of the  $^2E'$  states for distorted  $C_s$  geometries where both have  $^2A'$  local symmetry, restricts our choice of method effectively to the variational multireference configuration interaction (MR-CI) procedure. For efficiency we use a complete active space (CAS-SCF) for the reference wave functions and the internally contracted singles and doubles CI, as implemented in the MOLPRO<sup>14</sup> program package. The whole set of geometries is treated with an active space spanned by the orbital set from  $2a_1'$  to  $1e''$ ; extended calculations for a subset of  $C_{2v}$  geometries use an active space that includes the  $4e'$  and  $1a_2'$  orbitals as well. The basis set is constructed from the augmented correlation-consistent valence triple zeta (aug-cc-pVTZ) set for the B atom,<sup>15</sup> further augmented by two  $s$  functions (exponents 0.7 and 0.23) and one  $p$  set (exponent 0.35) at the bond centers. Comparison between experiment and theory for  $B_2$  suggests that this computational procedure supports an accuracy of about 0.02 bohr in bond lengths and about  $20\text{ cm}^{-1}$  in vibrational frequencies. These calculations have been performed for a grid of geometries which was defined by bond length variations in steps of 0.05 bohr, starting from the reference bond length of  $r = 3.00$  bohr and extending to all geometries for which one of the relevant electronic energies was less than  $3000\text{ cm}^{-1}$  above the corresponding reference energy.

The adiabatic PES's have been cast in analytical form by least-squares fits to polynomials in the symmetric stretch and radial deformation coordinates and harmonic functions of the azimuthal deformation coordinate, as described in previous work on alkali trimers.<sup>16,17</sup> In contrast to the alkali trimers, Jahn-Teller distortion in the lower  $E'$  states of  $B_3$  and  $B_3^-$  is weak as compared to vibrational excitation, so that both sheets of the PES for degenerate  $E$  states are substantially populated even for low vibrational energies. In order to avoid the notorious complications caused by the geometric phase in an adiabatic treatment, we use a diabatic framework for the vibrational motion, i.e., diabatic surfaces are constructed from the adiabatic ones by means of  $2 \times 2$  rotations with

angles  $\phi/2$ , where  $\phi$  is the pseudo-rotational coordinate. Hyperspherical coordinates are still the proper choice for a cyclic trimer but the computational procedures used previously<sup>18</sup> had to be extended to account for pairs of coupled diabatic surfaces. Both, the analytical fits and the vibrational calculations introduce numerical errors in the order of only  $1\text{ cm}^{-1}$  for the first transition in  $B_3$ , i.e., considerably smaller errors than those from the electronic structure calculations. For the other upper states our fits with standard errors of about  $10\text{ cm}^{-1}$  are only preliminary because of complications from additional conical intersections and/or notorious intruder state problems which cause unphysical humps in the upper state surfaces in particular for  $B_3^-$ .

Vibrational line intensities are calculated from transition dipole moment surfaces which are again expanded in polynomials as outlined above for the PES. Because the observed bands stem from in-plane transition moments (parallel bands), vibronic selection rules leave only  ${}^2E'$  vibronic states accessible in the case of free  $B_3$ . The degree of violation of this selection rule due to matrix effects is difficult to assess.

A sensible assignment of vibronic states by some kind of vibrational quantum numbers is difficult in cases of strong vibronic coupling, i.e., if linear and quadratic Jahn–Teller (JT) terms are of comparable size. Reference can be made to two simple limiting cases: (i) Strong quadratic terms produce three equivalent minima on the lower (adiabatic) surface which are separated by a relatively high barrier. The vibrational wave functions for the lower sheet can then be considered a linear combination of three equivalent local vibrators with  $C_{2v}$  symmetry placed at the respective minima and can be labeled by  $C_{2v}$  quantum numbers  $v_1$ ,  $v_2$ , and  $v_3$  for symmetric stretch, symmetric bend and asymmetric stretch, respectively. (ii) Weak quadratic JT terms produce only negligible localizing barriers for the pseudorotational motion. Then the quantum numbers for a free internal rotation are adequate, i.e.,  $v_1$ ,  $v_2$  for symmetric stretch and deformation and  $l_2$  for the pseudorotation angular momentum. In an adiabatic frame,  $v_2$  and  $l_2$  are half integer numbers due to the geometric phase in electronic and vibrational factors of the vibronic wave function. The finger print for case (i) is a near degeneracy of  $E-A$  pairs, that for case (ii) is a near degeneracy of  $A_1-A_2$  pairs. The actual assignment of model quantum numbers is made by inspection of plots of the vibrational wave functions. The model following case (i) has been successfully used for rovibronic analysis of alkali trimer  $E'' \leftarrow E'$  transition bands;<sup>16–18</sup> a thorough discussion of this model has been given there. Further details of our computational procedures may be found elsewhere.<sup>13</sup>

## V. ASSIGNMENT AND DISCUSSION

Our CAS-SCF calculations of vertical electronic transition energies at the  $D_{3h}$  reference geometry (bond length 3.00 bohr) reproduce the ordering of states as previously obtained, also from CAS-SCF:<sup>9</sup>  $X^2A'_1$ ,  $1^2A'_2$ ,  $1^2E'$ ,  $1^4E''$ ,  $1^4E'$ ,  $1^2E''$ ,  $2^2E'$ ,  $1^4A'_1$ ,  $1^4A'_2$ ... Pertinent data of the PESs, as obtained in the MR-CI calculations for the states relevant here, are collected in Table IV. Figure 3 shows cuts

TABLE IV. Transition energies, Jahn–Teller distortion energies and equilibrium geometries for selected states of  $B_3$  from MR-CI with the large active space (energies in  $\text{cm}^{-1}$ , distances in bohr and angles in degree).

State:	$1^2A'_1$	$1^2E'$	$2^2E'$
$T_v$		13 781	22 291
$T_e$		13 057	22 202
$T_{00}$		12 829	22 272
ZPE	1457	1207	1522
$E_{\text{stab}}$		475	39
$E_{\text{loc}}$		187	9
$r_{\text{min}}$	2.968	2.982	3.015
$\theta_{\text{min}}$	60.0	65.3	61.9
$r_{\text{sadd}}$		3.093	2.982
$\theta_{\text{sadd}}$		57.2	60.9

of these potentials for the bending deformation mode, which illustrate in particular the Jahn–Teller distortions in the  $E'$  states. The JT stabilization in the  $1^2E'$  state of  $475\text{ cm}^{-1}$  is on the order of stabilizations observed for alkali trimer  ${}^2E''$  states, but it amounts to little more than 1/3 of the zero point energy and only about 2/3 of the deformation mode energy quantum. The pseudorotational barrier between the three equivalent minima is only  $187\text{ cm}^{-1}$  but it is sufficiently broad to effectively lift the  $A_1/A_2$  degeneracy, indicating a case (i) description of the vibronic states. In contrast, for the  $2^2E'$  state with stabilization and localization energies of only 39 and  $9\text{ cm}^{-1}$ , respectively,  $B_3$  can be considered as

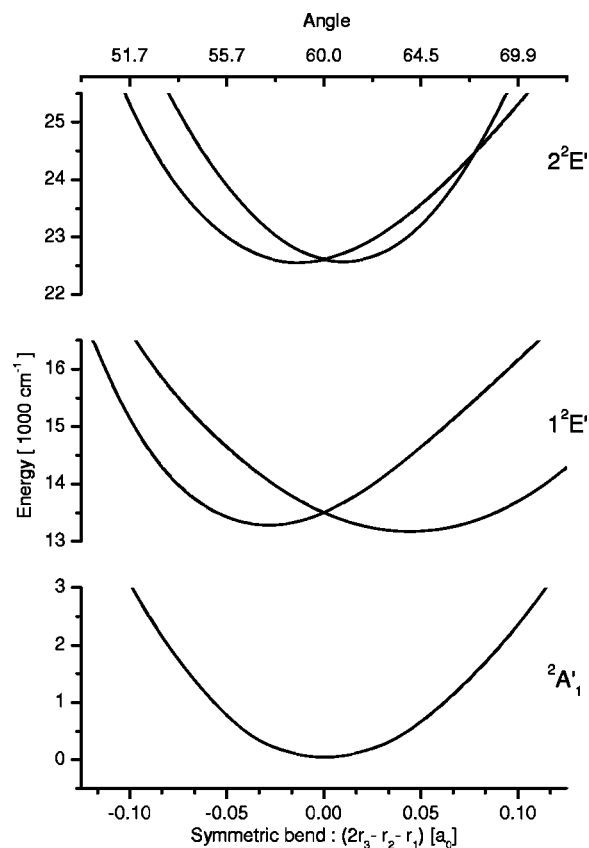


FIG. 3. One-dimensional cuts of the PESs along the bend coordinate for  $C_{2v}$  geometries with  $(r_1 + r_2 + r_3)/3 = 3.00$  bohr for the  $X^2A'_1$  and the two  ${}^2E'$  electronic states of  $B_3$ .

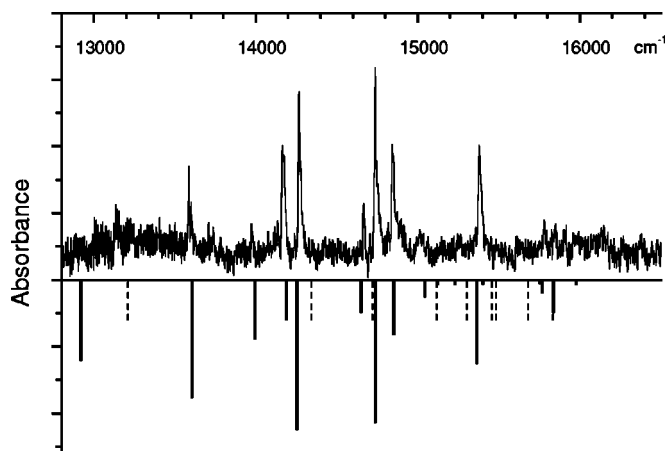


FIG. 4. Comparison of the calculated positions and intensities of the Jahn–Teller coupled vibronic levels for the  $1^2E'$  state of  $B_3$  with the matrix spectrum.

nearly freely pseudo-rotating, indicating a case (ii) description. This state has a second conical intersection of its two electronic components at  $C_{2v}$  geometries with apex angles around  $68^\circ$ . Such a feature causes severe complications for the fitting of a PES. Our present analytical potential is reliable only below that crossing and furnishes but a few low-lying vibrational levels. The shapes of these PES, and even more so the rather unexpected shapes of the transition moment surfaces, are consequences of the strong mixing of the two configurations that are formed by the  $3e' \leftarrow 3a'_1$  and the  $3a'_1 \leftarrow 2e'$  excitations. Actually, at the  $D_{3h}$  reference geometry the mixing ratios are 62:58 and 61:59 for the  $1^2E'$  and  $2^2E'$  states, respectively. The corresponding dipole transition moments of 0.137 and 0.253 a.u., respectively, indicate a clear difference in the intensities of the two bands, as is indeed observed.

The calculated positions of the transition bands are crucial for the assignment of electronic symmetries. We find the  $1^2E'$  band origin,  $T_{00}$ , at  $12\,829\text{ cm}^{-1}$  from the MR-CI with extended reference space. The corresponding results from the smaller MR-CI and from a Davidson correction are  $12\,988$  and  $12\,728\text{ cm}^{-1}$ , respectively, indicating an uncertainty in  $T_{00}$  of about  $250\text{ cm}^{-1}$ . However, the observed spectrum starts with a line at  $13\,587\text{ cm}^{-1}$ , which is  $752\text{ cm}^{-1}$  higher than calculated. This difference is too large to be attributed to matrix effects. It is not only larger than the estimated uncertainty, but its sign is unlikely since in variational calculations excited-state energies are usually less well accounted for than ground-state energies. This suggests that the first observed line is not the band origin but corresponds to the first excited vibrational level. This is indeed supported by the positions and intensities calculated for the higher vibrational states, as obvious from Fig. 4, where the observed spectrum is compared with the theoretical one, the latter shifted only by  $30\text{ cm}^{-1}$ . Agreement appears to be rather satisfactory considering the well-known fact that matrix effects may affect the band positions and in particular their intensities. The triplet feature seen in the center of the spectrum belongs to vibrational states that are heavily mixed, so that the calculated intensities may well need some redistribution, since the com-

position of the vibronic wave functions is computationally more sensitive to the accurate description of the coupling than the vibronic energies. However, this assignment of the vibrational structure is in conflict with the fact that the observed spectrum does not show a line with significant strength at the predicted position of the band origin. On the other hand, if the band origin is identified with the first strong observed line, we can not explain that two strong observed lines do not have theoretical counterparts and that a line with a strong calculated intensity is missing. It is difficult to see how matrix effects could be held responsible for this mismatch. A gas spectrum is necessary.

Table II lists observed and calculated vibrational energies and the calculated relative intensities, making also use of the theoretical first excitation energy to define the “true” band origin, which becomes  $12\,902\text{ cm}^{-1}$ . Figure 5 displays vibrational levels ordered according to vibronic symmetry and assigned with vibrational quantum numbers of a  $C_{2v}$  vibrator as outlined above. This assignment is reasonable for the lower levels but loses meaning for higher ones, in particular if levels are close and undergo substantial mixing. This is regularly the case for neighboring levels of polyads formed by replacing two quanta of symmetric bend by one quantum of asymmetric stretch. Note that only the levels of vibronic  $E$  character are accessible.

The calculated band origin for the  $2^2E'$  state of  $22\,272\text{ cm}^{-1}$  agrees fairly well with the observed position of the main line,  $21\,828\text{ cm}^{-1}$ . There is no other candidate close by. Vibrational energy levels, which are only preliminary in this case due to problems with the fit of the PES, are included in Table III. The observed line positions may be nicely lined up with calculated values but this is not really definitive as long as theoretical intensities are lacking for this state. While the ground vibrational state is 93%  $a'_1$ , the first upper state is 60%  $e'_1$  and 30%  $a'_1$ , i.e., the progression observed involves mainly the deformation mode with only zero-point pseudorotation. The proper assignment according to case (ii) is  $(0\ 1/2\ 1/2)$ ,  $(0\ 3/2\ 1/2)$ , and  $(0\ 5/2\ 1/2)$  for the three levels involved.

For the  $1^2A'_2$  state we calculate a vertical excitation energy  $T_v$  of  $6300\text{ cm}^{-1}$ . This region was inaccessible in the experiments carried out hitherto. As a general comment on the transition energies, we note that dynamical electron correlation, accounted for only by the singles–doubles CI build on top of the CAS-SCF, causes changes of up to  $2000\text{ cm}^{-1}$ . Comparison to previously published theoretical excitation energies, which are limited to CAS-SCF, shows indeed differences of this order.<sup>8</sup>

In the case of the  $B_3^-$  anion the calculated adiabatic excitation energy  $T_e$  of  $23\,089\text{ cm}^{-1}$  differs from the observed band origin at  $21\,413\text{ cm}^{-1}$  by  $1676\text{ cm}^{-1}$ . Less than  $300\text{ cm}^{-1}$  may be attributed to the change in the zero point energy (ZPE), leaving a defect of around  $1400\text{ cm}^{-1}$ . Extension of our basis set by diffuse functions, which might be important for an excited state of an anion, reduces this defect by only about  $100\text{ cm}^{-1}$  but the Davidson correction yields a surprisingly large further reduction of about  $800\text{ cm}^{-1}$  in this case. The assignment to the  $1^1E' \leftarrow X^1A'_1$  electronic transition of cyclic  $B_3^-$  is not questioned since no other candidates are available. A vibrational analysis of this transition has to

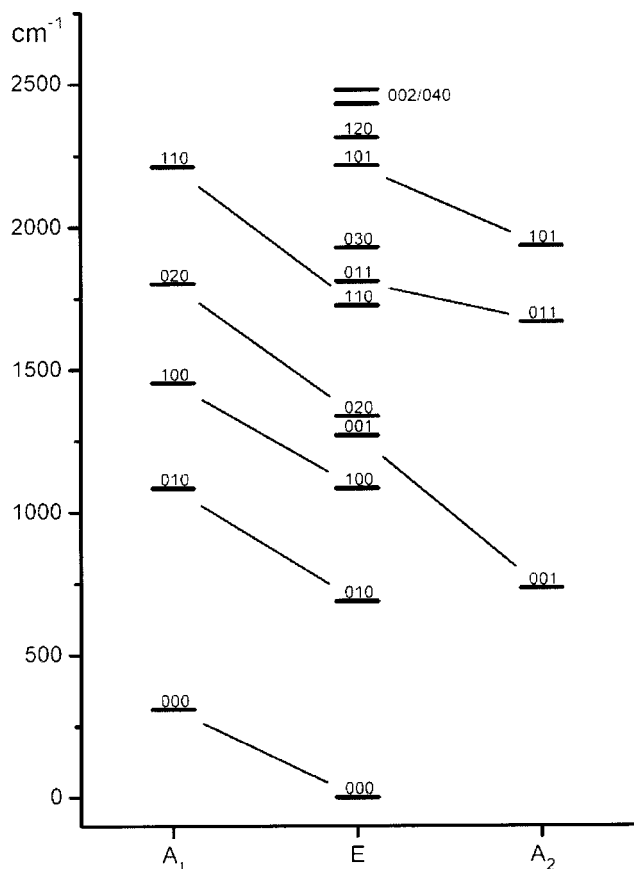


FIG. 5. Pattern of Jahn-Teller coupled vibronic levels of the  $1^2E'$  state in  $B_3$ . For the definition of the modes see text.

be deferred until a better analytic representation of the upper state PES is available.

## VI. CONCLUSION

The matrix isolation technique in combination with mass selection has been applied to observe for the first time the electronic spectra of the boron trimer and its anion. As a result, the  $1^2E' \leftarrow X^2A'_1$  and the  $2^2E' \leftarrow X^2A'_1$  electronic transitions for  $B_3$  and  $1^1E' \leftarrow X^1A'_1$  for  $B_3^-$  have been identified. The vibronic structure of the  $1^2E'$  electronic state of the neutral species and the  $1^1E'$  state of the anion exhibit a strong influence of the Jahn-Teller effect. *Ab initio* calculations of potential energy surfaces for four electronic states of  $B_3$  and two electronic states of  $B_3^-$  have validated the assignment of the observed bands and provided the basis for an

analysis of the vibrational structure of the transition to the  $1^2E'$  state of a free  $B_3$ . The observed pattern can be considered as well reproduced if the true origin of the transition is placed at about  $12\,900\text{ cm}^{-1}$  where no significant absorption line is seen. An in-depth analysis will require high resolution gas-phase measurements and theory developments. The present work provides the necessary basis for these to be undertaken.

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# Gas phase detection of cyclic B<sub>3</sub>: 2<sup>2</sup>E' ← X<sup>2</sup>A<sub>1</sub>' electronic origin band

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The rotationally resolved origin band in the 2<sup>2</sup>E' ← X<sup>2</sup>A<sub>1</sub>' electronic spectrum of cyclic B<sub>3</sub> has been observed by cavity ring down spectroscopy in the gas phase. The B<sub>3</sub> molecule was generated in a supersonic planar plasma containing decaborane (B<sub>10</sub>H<sub>14</sub>) and neon as a carrier gas. The rotational structure pattern is that of a cyclic molecule. It is analyzed assuming an equilateral triangle in both electronic states. The band origin is determined to be 21 853.52 cm<sup>-1</sup>, and the bond lengths 1.603 77(106) Å in the ground and 1.619 07(96) Å in the excited electronic state are inferred from analysis of the rotational structure. © 2004 American Institute of Physics.  
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## I. INTRODUCTION

Well resolved absorption and emission spectra of cyclic trimers have been reported only for few species, including, Al<sub>3</sub>,<sup>1</sup> Li<sub>3</sub>,<sup>2</sup> Cu<sub>3</sub>,<sup>3</sup> H<sub>3</sub><sup>+</sup>,<sup>4</sup> and Na<sub>3</sub>.<sup>5</sup> As the small boron molecules have applications in industry as chemical insulators, explosives, semiconductors, and high energy density materials, their structure is of relevance.<sup>6,7</sup> The boron trimer has been investigated only in rare gas matrices. First came the electron-spin-resonance observation which showed that B<sub>3</sub> contains an unpaired electron and that the three nuclei are equivalent.<sup>8</sup> The infrared spectrum of B<sub>3</sub> was also observed,<sup>1</sup> and recently the 2<sup>2</sup>E' ← X<sup>2</sup>A<sub>1</sub>' electronic transition of B<sub>3</sub> in a neon matrix was identified using a mass selective approach.<sup>9</sup> However, there is no spectroscopic information on the boron trimer B<sub>3</sub> in the gas phase.

There is interest in the spectrum of cyclic B<sub>3</sub> because several of the excited electronic states are degenerate in D<sub>3h</sub> symmetry. According to the Jahn-Teller theorem, there exists at least one vibrational mode that removes the electronic degeneracy and results in the stabilization of the lowest component by lowering the symmetry of the equilibrium structure. Most recent theoretical calculations on B<sub>3</sub> predicted an equilateral structure (D<sub>3h</sub>) with an <sup>2</sup>A<sub>1</sub>' electronic symmetry in the electronic ground state and an obtuse triangle (C<sub>2v</sub>) with an apex angle ≥60° for the 2<sup>2</sup>E' excited electronic state.<sup>8,10,11</sup> However, a low stabilization energy (difference between the conical intersection and the minima) compared with zero point energy for the 2<sup>2</sup>E' state is reported.<sup>9</sup> Therefore the B<sub>3</sub> molecule can be considered to have D<sub>3h</sub> symmetry in the 2<sup>2</sup>E' state as an effective structure and the 2<sup>2</sup>E' ← X<sup>2</sup>A<sub>1</sub>' electronic system can be considered as a quasi "D<sub>3h</sub>-D<sub>3h</sub>" transition.

In the present work we report the observation of the rotationally resolved origin band of the 2<sup>2</sup>E' ← X<sup>2</sup>A<sub>1</sub>' electronic spectrum of B<sub>3</sub>. The analysis of the spectrum gives an estimate of the molecular geometry; the first gas phase structural determination.

## II. EXPERIMENT

This consists of a standard cavity ring down setup sampling a plasma generated in a pulsed supersonic slit jet expansion.<sup>12</sup> A small fraction of pulsed laser light from a tunable dye laser is coupled into an optical cavity consisting of two highly reflective mirrors (*R* > 99.99%). The fraction of light leaking out of the cavity has an envelope which is a first-order exponential decay, exp(−*t*/τ). The ring down time τ reflects the absorption coefficient. A spectrum is recorded by measuring τ as function of the wavelength of the laser (running at 30 Hz). Forty-five ring down events are averaged at each wavelength before the digitized data are downloaded to a workstation. The ~0.05 cm<sup>-1</sup> linewidth of the laser was attained with an internal etalon.

The pulsed slit jet system is located in a vacuum chamber evacuated by a roots blower. The plasma is produced in a nozzle incorporating a discharge in the high pressure expansion. The orifice comprises a metal plate anode and two sharp stainless steel cathodes that form the actual slit (30 mm × 300 μm). A pulsed negative voltage (−800 V/100 mA and 100 μs in duration) is applied. The geometry of the orifice is such that the discharge is confined upstream of the supersonic expansion. To produce B<sub>3</sub>, solid B<sub>10</sub>H<sub>14</sub> is heated in the oven to 70 ± 10 °C with neon as a carrier gas at a backing pressure of 10 bars. In order to avoid condensation inside the source, the valve and body of the nozzle are heated as shown in Fig. 1. The B<sub>3</sub> molecules are efficiently produced at a distance 5 mm down stream from the slit. The spectrum is calibrated via the neon atomic lines that are observed in the jet expansion.

## III. RESULTS

The 2<sup>2</sup>E' ← X<sup>2</sup>A<sub>1</sub>' electronic spectrum of B<sub>3</sub> was initially identified in absorption in a 6 K neon matrix using mass selection with origin band located at 21 828 cm<sup>-1</sup>.<sup>9</sup> Based on this the band was sought in the gas phase. The absorption signal was subsequently found near 21 900 cm<sup>-1</sup> (Fig. 2) and the observed profile of the band, ~25 cm<sup>-1</sup> in width, was in a good agreement with preliminary simulations. No other signal could be detected within ±300 cm<sup>-1</sup>

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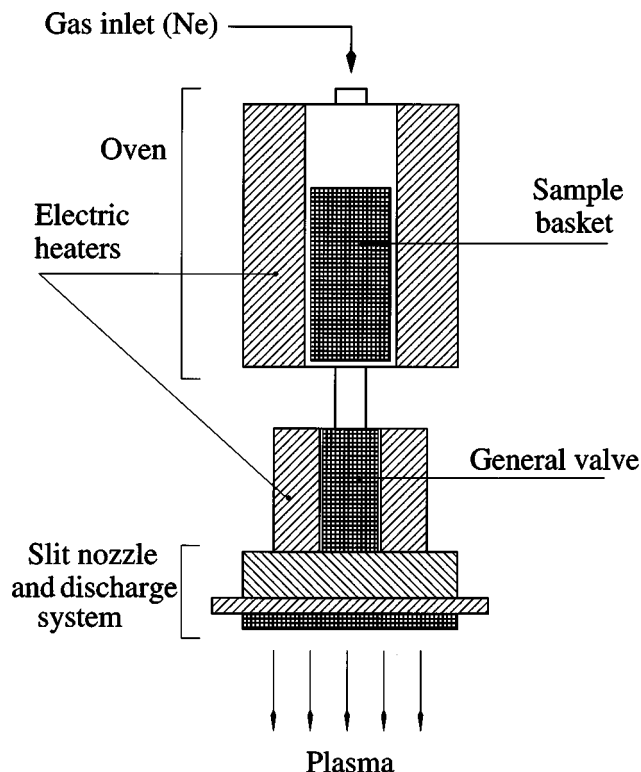


FIG. 1. Schematic diagram of the source used to produce B<sub>3</sub>. Decaborane was heated up to  $70 \pm 10$  °C in the oven. Neon at a backing pressure of 10 bars was used as a carrier gas. The pulsed plasma was produced by a slit nozzle to which the high voltage was applied.

from the observed band. Though the spectrum visually appears “noisy” (typical  $S/N$  of at least 5) all the peaks are genuine. This is shown by the top trace which is an independent recording of this part of the band. Corresponding traces were obtained for other regions proving that all the lines given in Tables I and III are real.

The spectrum exhibits rotationally resolved  $P$  and  $R$  branches slightly blended with strong neon atomic lines. The  $Q$  branch is not visible due to a complex splitting and blending with an intense neon line. Actually, it is a composition of four spectra, as two boron isotopes are present. Because the natural isotopic abundance of  $^{11}\text{B}$ : $^{10}\text{B}$  in the precursor is 4:1, the relative concentration of the two isotopomers  $^{33}\text{B}_3$ : $^{32}\text{B}_3$  (two equivalent structures of  $^{10}\text{B}^{11}\text{B}_2$ ) should be 4:3. The peaks in the spectra of  $^{31}\text{B}_3$  and  $^{30}\text{B}_3$  could not be assigned due to their small abundance. As a result, the observed spectrum is essentially an overlap of the two isotopomers  $^{33}\text{B}_3$  and  $^{32}\text{B}_3$ .

The B<sub>3</sub> cyclic molecule in the excited degenerate state should undergo a deformation due to the Jahn-Teller effect, however, the distortion from an equilateral triangle can be neglected as a result of low stabilization energy [merely  $39\text{ cm}^{-1}$  compared with a zero-point energy ( $1522\text{ cm}^{-1}$ ) in the  $2^2E'$  state<sup>9</sup>]. A similar situation was encountered for the cyclic C<sub>3</sub>H radical, where deformations of the C<sub>2v</sub> structure were neglected due to small energy differences between the C<sub>s</sub> and C<sub>2v</sub> forms.<sup>13</sup> Therefore, it is reasonable to assume that the effective symmetry of the  $2^2E'$  state is  $D_{3h}$  for the analysis of the rotational structure in the observed spectrum.

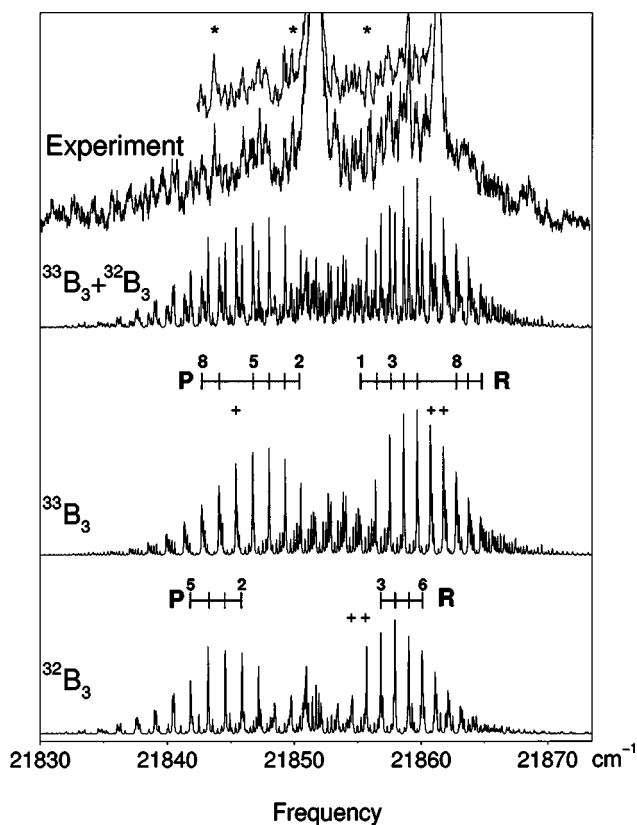


FIG. 2. Rotationally resolved  $2^2E' \leftarrow X^2A'_1$  electronic origin band of B<sub>3</sub> in the gas phase measured by cavity ring down spectroscopy through a supersonic planar plasma. The two upper traces are independent recordings to show that the peaks are real and not noise. The three bottom traces are the simulated patterns  $^{33}\text{B}_3 + ^{32}\text{B}_3$  (in ratio 4:3),  $^{32}\text{B}_3$  and  $^{33}\text{B}_3$ . The two strong lines off scale belong to neon. Bands marked with \* are unassigned. Lines in the simulation for which counterparts in the spectrum could not be found are marked with “+.”

The measured positions of the  $^{33}\text{B}_3$  lines are given in Table I. The spectral line frequencies were analyzed using a conventional Hamiltonian for a symmetric top molecule. In order to analyze the imperfectly resolved rotational spectrum it was assumed that the structure of the B<sub>3</sub> molecule has  $D_{3h}$  symmetry in both states. This way the number of spectro-

TABLE I. Frequencies (in  $\text{cm}^{-1}$ ) and assignments in the  $2^2E' \leftarrow X^2A'_1$  absorption spectrum of  $^{33}\text{B}_3$ .

$N_K$	$\nu_{\text{obs}}$	$\nu_{\text{calc}}$	$\nu_{\text{obs}} - \nu_{\text{calc}}$
1 <sub>1</sub> -2 <sub>2</sub>	21 850.374	21 850.543	-0.169 <sup>a</sup>
2 <sub>2</sub> -3 <sub>3</sub>	21 849.223	21 849.296	-0.073
3 <sub>3</sub> -4 <sub>4</sub>	21 848.070	21 848.027	0.043
4 <sub>4</sub> -5 <sub>5</sub>	21 846.731	21 846.736	-0.005
6 <sub>6</sub> -7 <sub>7</sub>	21 844.118	21 844.086	0.032
7 <sub>7</sub> -8 <sub>8</sub>	21 842.710	21 842.727	-0.017
1 <sub>1</sub> -0 <sub>0</sub>	21 855.230	21 855.305	-0.075
2 <sub>2</sub> -1 <sub>1</sub>	21 856.499	21 856.440	0.059
3 <sub>3</sub> -2 <sub>2</sub>	21 857.600	21 857.552	0.048
4 <sub>4</sub> -3 <sub>3</sub>	21 858.629	21 858.642	-0.013
5 <sub>5</sub> -4 <sub>4</sub>	21 859.690	21 859.710	-0.020
8 <sub>8</sub> -7 <sub>7</sub>	21 862.770	21 862.778	-0.008
9 <sub>9</sub> -8 <sub>8</sub>	21 863.713	21 863.756	-0.043
10 <sub>10</sub> -9 <sub>9</sub>	21 864.749	21 864.712	0.037

<sup>a</sup>Not included in the least-squares fit.

TABLE II. Bond lengths and spectroscopic constants of the  $^{33}\text{B}_3$  molecule inferred from the partial rotational analysis of the  $2^2E' \leftarrow X^2A'_1$  electronic origin band.<sup>a</sup>

	$2^2A'_1$		$2^2E'$	
	Obs.	Calc. <sup>b</sup>	Obs.	Calc. <sup>b</sup>
$r_0$ (Å)	1.603 77(106)		1.619 07(96)	
$\theta_0$ (deg)	60.0 <sup>c</sup>		60.0 <sup>c</sup>	
$r_e$ (Å)		1.5706		1.5955
$\theta_e$ (deg)		60.0		60.8
$T_{00}$ (cm <sup>-1</sup> )			21 853.52 <sup>d</sup>	22 723
$B$ (cm <sup>-1</sup> )	1.190 64(157) <sup>e</sup>		1.168 25(138) <sup>e</sup>	
$C$ (cm <sup>-1</sup> )	0.595 32(79) <sup>e</sup>		0.584 12(69) <sup>e</sup>	

<sup>a</sup>The numbers in parentheses represent the one standard deviation derived from the least square fitting. A rms of the fitting is 0.043 cm<sup>-1</sup>.

<sup>b</sup>Reference 9.

<sup>c</sup>Fixed.

<sup>d</sup>Error of calibration is around 0.01 cm<sup>-1</sup>.

<sup>e</sup>The rotational constants were calculated from the determined molecular structures.

scopic parameters could be reduced to 3; the bond lengths  $r'$ ,  $r''$  and band origin  $T_{00}$  were then determined directly from a least-squares fit to the line positions.

The results for the  $^{33}\text{B}_3$  molecule are listed in Table II. The determined bond lengths ( $r_0$ ) are 2% longer than the calculated ones ( $r_e$ ) (Ref. 9) in both the ground and excited states. In the ground state this is because of zero-point vibrations as the analysis assumes a negligible inertial defect. The difference in the excited state is additionally caused by imperfections of the simple model used (assuming an equilateral triangle  $\theta=60^\circ$  and ignoring the Jahn-Teller effect) and anharmonicity of the potential.

The observed rotational profile was also simulated with the obtained molecular constants using the program WANG.<sup>14</sup> The simulated spectrum of  $^{33}\text{B}_3$  is shown in Fig. 2. Best agreement with the experiment was attained with a rotational temperature of 30 K. A linewidth of 0.05 cm<sup>-1</sup> was used for the simulation, though in the observed spectrum it is larger due to Doppler and/or lifetime broadening.

In the case of the  $^{32}\text{B}_3$  isotopomer the simulation was based on the same geometry and temperature parameters as inferred for  $^{33}\text{B}_3$  but using a conventional Hamiltonian of an asymmetric top molecule. It was also assumed that only the  $B_2-A_1$  transition, which is a type, occurs. The rotational constants used for the  $^{32}\text{B}_3$  molecule were  $A:B:C=1.2696:1.1906:0.6144$  cm<sup>-1</sup> for the ground, and  $1.2457:1.1682:0.6029$  cm<sup>-1</sup> for the excited state. The spectrum of  $^{32}\text{B}_3$  was then shifted by  $-1.94$  cm<sup>-1</sup> (from  $T_{00}$  of  $^{33}\text{B}_3$ ) to get the best agreement with the observation (Fig. 2). The isotopic shift of  $-1.94$  cm<sup>-1</sup> is reasonable for an origin band.

In all, 34 rotational transitions were assigned; 14 of them are attributed to the  $^{33}\text{B}_3$  molecule and the rest to  $^{32}\text{B}_3$  (Table III). The presented rotational assignment and molecular structure of the  $\text{B}_3$  molecule should be considered as tentative, because the insufficient  $S/N$  ratio of the spectrum decreases the accuracy of the molecular structure determina-

TABLE III. Frequencies (in cm<sup>-1</sup>) and assignments in the  $2^2E' \leftarrow X^2A'_1$  absorption spectrum of  $^{32}\text{B}_3$ .<sup>a</sup>

$N_{K_a K_c}$	$\nu_{\text{obs}}$	$\nu_{\text{calc}}$	$\nu_{\text{obs}} - \nu_{\text{calc}}$
2 <sub>12</sub> -3 <sub>13</sub>	21 847.174	21 847.197	-0.023
2 <sub>02</sub> -3 <sub>03</sub>		21 847.183	-0.009
3 <sub>13</sub> -4 <sub>14</sub>	21 845.859	21 845.877	-0.018
3 <sub>03</sub> -4 <sub>04</sub>		21 845.876	-0.017
4 <sub>14</sub> -5 <sub>15</sub>	21 844.525	21 844.544	-0.019
4 <sub>04</sub> -5 <sub>05</sub>			
5 <sub>15</sub> -6 <sub>16</sub>	21 843.220	21 843.188	0.032
5 <sub>05</sub> -6 <sub>06</sub>			
6 <sub>16</sub> -7 <sub>17</sub>	21 841.821	21 841.809	0.012
6 <sub>06</sub> -7 <sub>07</sub>			
7 <sub>17</sub> -8 <sub>18</sub>	21 840.420	21 840.407	0.013
7 <sub>07</sub> -8 <sub>08</sub>			
4 <sub>14</sub> -3 <sub>13</sub>	21 856.843	21 856.832	0.011
4 <sub>04</sub> -3 <sub>03</sub>		21 856.833	0.010
5 <sub>15</sub> -4 <sub>14</sub>	21 857.952	21 857.934	0.018
5 <sub>05</sub> -4 <sub>04</sub>			
6 <sub>16</sub> -5 <sub>15</sub>	21 859.041	21 859.013	0.028
6 <sub>06</sub> -5 <sub>05</sub>			
7 <sub>17</sub> -6 <sub>16</sub>	21 860.125	21 860.068	0.057
7 <sub>07</sub> -6 <sub>06</sub>			

<sup>a</sup>The assignment and calculated frequencies were derived on the assumption that the bond lengths of  $^{32}\text{B}_3$  and  $^{33}\text{B}_3$  are equal, and the isotopic shift is  $-1.94$  cm<sup>-1</sup>.

tion. Lines of  $^{31}\text{B}_3$  ( $\approx 19\%$  of the  $^{33}\text{B}_3$  intensity) disturb the line profiles of  $^{32}\text{B}_3$  and  $^{33}\text{B}_3$  transitions. There are few unassigned lines, few missing ones, and some are obscured by intense neon atomic lines (Fig. 2). However, the consistency of the whole analysis is sufficient to conclude that the observed rotationally resolved spectrum is indeed the  $2^2E' \leftarrow X^2A'_1$  transition of the cyclic  $\text{B}_3$  molecule, and leads to the first structural information in the gas phase.

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# The near infrared $1^2A_2'' \leftarrow X^2A_1'$ electronic transition of $B_3$ in a neon matrix

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## Abstract

The  $1^2A_2'' \leftarrow X^2A_1'$  electronic transition of the  $B_3$  molecule with origin band at  $5990\text{ cm}^{-1}$  has been observed in a 6 K neon matrix. A vibrational progression in the spectrum corresponds to the excitation of the  $\nu_1(a_1')$  vibrational mode in the  $1^2A_2''$  state with a frequency of  $\sim 1092\text{ cm}^{-1}$ . The band system was detected after laser ablation of a boron rod and the origin band also after mass-selected deposition of  $B_3^-$  anions with subsequent neutralization.

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## 1. Introduction

Structure and properties of boron clusters are interesting for fundamental science. Boron is the only element except carbon that can build molecules of any size by covalent bonds, and there are a number of applications [1,2]. Nevertheless, even molecules as small as  $B_3$  are spectroscopically not thoroughly investigated. The first study of  $B_3$  was by ESR [3] followed by IR spectroscopy [4] both in rare gas matrices. A previous publication reported the  $1^2E' \leftarrow X^2A_1'$  and  $2^2E' \leftarrow X^2A_1'$  electronic transitions of  $B_3$  in a 6 K neon matrix [5]. The rotationally resolved origin band of the  $2^2E' \leftarrow X^2A_1'$  transition has been measured since then in absorption in the gas phase and analyzed [6]. Ab initio calculations on the ground and excited electronic states of  $B_3$  are available [5,7]. In the present work the  $1^2A_2'' \leftarrow X^2A_1'$  electronic transition of  $B_3$  has been observed for the first time in a 6 K neon matrix.

## 2. Experimental

The main features of the experimental set up have been described [8]. Two approaches were used to produce boron clusters: one with a cesium sputter ion source and the other by laser ablation. Boron rod (99.6% purity) with a natural isotopic composition was used as a target for the laser vaporization.  $B_4C$ ,  $LaB_6$  and BN rods were used as well.

A slowly rotating sample rod was installed  $\sim 10\text{ cm}$  from the matrix substrate. A 532-nm pulsed Yag laser beam,  $\sim 20\text{ mJ}$ , 20 Hz, was focused on the rod. A mixture of ionic and neutral ablation products was co-deposited with excess of neon (or argon) onto a sapphire substrate coated with rhodium and cooled to a temperature of 6 K. Spectra in the  $1100\text{--}12000\text{ cm}^{-1}$  range were recorded after sampling the neon matrix by a Fourier transform spectrometer applying a double reflection technique. The light beam reflects from the metal surface of the substrate on which the neon matrix sits, then from a mirror into the matrix again and back from the substrate. Absorption spectra in the 220–1100 nm region have been measured by passing monochromatic light through the matrix in a wave-guide manner [9].

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In order to assign the observed band system, experiments with mass-selected boron anions, produced in a cesium sputter source [10] have been carried out. The anions produced in the source were guided by means of electrostatic lenses into the quadrupole mass filter and were separated from neutral molecules by deflecting the beam through 90°. The  $B_3^-$  ions were mass selected and co-deposited with excess of neon to form a matrix at  $\sim 6$  K. A typical current of  $B_3^-$  impinging on the matrix was  $\sim 5$  nA. This technique allowed the deposition of  $B_3^-$  exclusively but it was not possible to obtain a high concentration of neutral  $B_3$  in the matrix.

Neutral  $B_3$  was produced by irradiation of the matrix with a mercury medium pressure lamp during  $\sim 30$  min. An important procedure was annealing up to 8.5 K making the neon matrix softer and thus allowing relaxation of the trapped molecules to their energetic minima (and even some reactions to proceed).

### 3. Observations

Several new bands were seen after laser vaporization of the boron rod in the infrared (Fig. 1), in addition to the previously reported  $1^2E' \leftarrow X^2A'_1$  and  $2^2E' \leftarrow X^2A'_1$  absorption systems of the  $B_3$  molecule [5,6] and those of the B and  $B_2$  species [11–13] in the visible and UV. The new system comprises three peaks, separated by  $\sim 1092$   $\text{cm}^{-1}$ , with origin band at  $5990$   $\text{cm}^{-1}$  (Table 1). This was seen after vaporization of  $B_4C$  and  $LaB_6$  rods as well. The intensity of the bands increases after irradiation of the matrix with UV photons indicating a neutralization process. Thus one can conclude that the carrier is a neutral boron molecule. The band system is not likely due to a boron and hydrogen (common

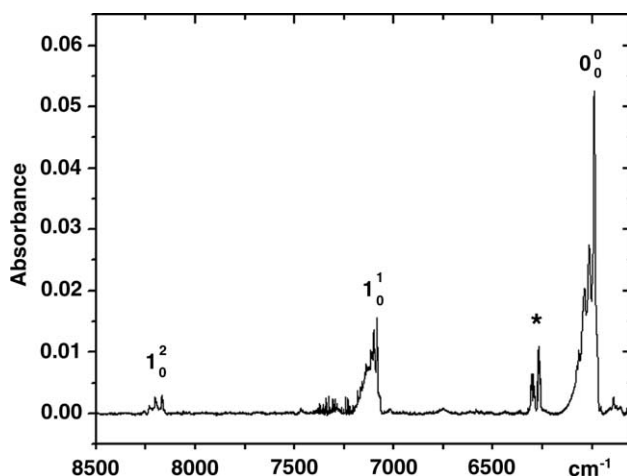


Fig. 1. The  $1^2A_2'' \leftarrow X^2A'_1$  electronic absorption spectrum of  $B_3$  in a 6 K neon matrix after laser vaporization of a pure boron rod. The band marked with \* is due to an unknown impurity.

Table 1

Positions of the band maxima ( $\pm 0.2$   $\text{cm}^{-1}$ ) in the  $1^2A_2'' \leftarrow X^2A'_1$  electronic transition of  $B_3$  in a 6 K neon matrix

$\nu$ ( $\text{cm}^{-1}$ )	$\Delta\nu$ ( $\text{cm}^{-1}$ )	Vibrational transition
5990	0	$0_0^0$
7085	1095	$1_0^1$
8169	2179	$1_0^2$

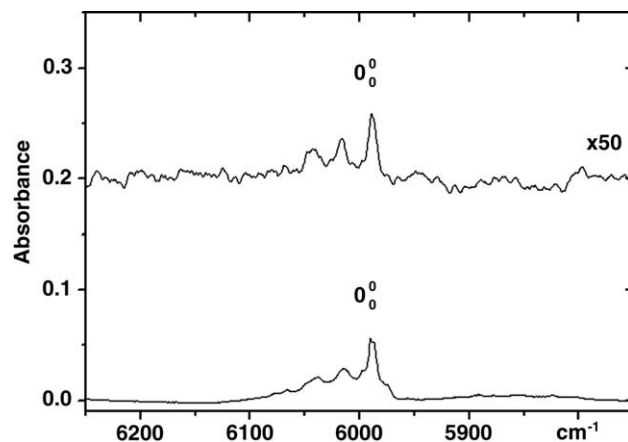


Fig. 2. The origin band of the  $1^2A_2'' \leftarrow X^2A'_1$  electronic absorption of  $B_3$  in a 6 K neon matrix after laser vaporization of a pure boron rod (lower trace), and after mass-selected deposition of  $B_3^-$  with subsequent neutralization by UV irradiation (upper trace – multiplied by a factor of 50 and smoothed).

impurity) containing species. When 1% of hydrogen was introduced into the matrix (Ne/ $H_2$  ratio of 100/1) the intensity of bands remained the same. The absorption band at  $6268$   $\text{cm}^{-1}$  (marked with \*) is due to an unknown impurity. Its intensity depended on the rod used.

Fine structure of the bands is due to matrix site effects. The trapped molecules have different orientations in the neon lattice. One can see that the three bands of the new system possess the same structure. After annealing to 8.5 K intensity redistribution is observed. The site-pattern is different when argon is used as the matrix.

Mass selected deposition of  $B_3^-$  followed by neutralization led also to the appearance of the  $5990$   $\text{cm}^{-1}$  absorption band (Fig. 2). The wavelength of the band and the site structure are exactly the same as in the laser vaporization spectrum. However, the intensity is about 50 times lower for the mass selected case. The bands at  $7085$  and  $8169$   $\text{cm}^{-1}$  corresponding to vibrational excitation in the upper electronic state were not observed in the mass-selected experiment due to a low signal to noise ratio. It is concluded that the observed system with the origin band at  $5990$   $\text{cm}^{-1}$  is an electronic transition of  $B_3$ .

#### 4. Discussion

It is theoretically established that  $B_3$  has an equilateral triangle structure ( $D_{3h}$  group) with  $^2A'_1$  symmetry in the ground state with electronic configuration  $(1a'_1)^2(1e')^4(1a''_2)^2(2a'_1)^1$  [5,7,14]. The only excited states accessible from the ground state by electric dipole transitions are  $^2A''_2$  and  $^2E'$ . The electronic transitions  $1^2E' \leftarrow X^2A'_1$  and  $2^2E' \leftarrow X^2A'_1$  of  $B_3$  in a neon matrix have been studied earlier [5]. The ab initio calculations predict that the transition to the lowest excited state with  $^2A''_2$  symmetry lies at  $\sim 6300\text{ cm}^{-1}$ ; in an earlier calculation  $7000\text{ cm}^{-1}$  was obtained [7]. These are energetically in good agreement with the observed origin band (Fig. 1). Consequently the new absorption system is assigned to the  $1^2A''_2 \leftarrow X^2A'_1$  dipole-allowed electronic transition of  $B_3$ .

$B_3^-$  has been studied by photoelectron spectroscopy [14] giving the vertical detachment energies of 2.82 and 3.56 eV to the  $B_3$  final states  $X^2A'_1$  and  $1^2A''_2$ . The 0.74 eV ( $\sim 6000\text{ cm}^{-1}$ ) difference between these is also in agreement with the present observations.

Equilateral triangular  $B_3$  molecule has two normal vibrations:  $a'_1$  and  $e'$ . Only transitions to the totally symmetric vibrational levels of the upper state ( $1^2A''_2$ ) are allowed from the  $X^2A'_1$  ground state, the solely populated level at 6 K. Hence the bands at 7085 and  $8169\text{ cm}^{-1}$  (Table 1) are assigned as the first two members of the progression structure associated with the  $a'_1$  normal mode excitation in the upper  $1^2A''_2$  state. The  $\nu_1(a'_1)$  frequency is thus inferred to be  $1092 \pm 3\text{ cm}^{-1}$ , in agree-

ment with the analysis of the photoelectron spectrum [14] of  $B_3^-$  which yielded the value  $1130 \pm 30\text{ cm}^{-1}$ .

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## Vibrations in the $B_4$ rhombic structure

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A double minimum six-dimensional potential energy surface (PES) is determined in symmetry coordinates for the most stable rhombic ( $D_{2h}$ )  $B_4$  isomer in its  $^1A_g$  electronic ground state by fitting to energies calculated *ab initio*. The PES exhibits a barrier to the  $D_{4h}$  square structure of  $255\text{ cm}^{-1}$ . The vibrational levels ( $J=0$ ) are calculated variationally using an approach which involves the Watson kinetic energy operator expressed in normal coordinates. The pattern of about 65 vibrational levels up to  $1600\text{ cm}^{-1}$  for all stable isotopomers is analyzed. Analogous to the inversion in ammonia-like molecules, the rhombus rearrangements lead to splittings of the vibrational levels. In  $B_4$  it is the  $B_{1g}$  ( $D_{4h}$ ) mode which distorts the square molecule to its planar rhombic form. The anharmonic fundamental vibrational transitions of  $^{11}B_4$  are calculated to be (splittings in parentheses):  $G(0)=2352(22)\text{ cm}^{-1}$ ,  $\nu_1(A_{1g})=1136(24)\text{ cm}^{-1}$ ,  $\nu_2(B_{1g})=209(144)\text{ cm}^{-1}$ ,  $\nu_3(B_{2g})=1198(19)\text{ cm}^{-1}$ ,  $\nu_4(B_{2u})=271(24)\text{ cm}^{-1}$ , and  $\nu_5(E_u)=1030(166)\text{ cm}^{-1}$  ( $D_{4h}$  notation). Their variations in all stable isotopomers were investigated. Due to the presence of strong anharmonic resonances between the  $B_{1g}$  in-plane distortion and the  $B_{2u}$  out-of-plane bending modes, the higher overtones and combination levels are difficult to assign unequivocally. © 2005 American Institute of Physics. [DOI: 10.1063/1.1828045]

### I. INTRODUCTION

Boron catenation leads to a large variety of stable structures which are of interest in many research areas and applications.<sup>1</sup> They have been the subject of numerous experimental<sup>2–9</sup> and theoretical<sup>10–28</sup> investigations.

Spectral data are still limited for pure boron clusters. Two electronic transitions of the  $B_2$  molecule have been observed in the gas phase<sup>8</sup> and in cold matrices.<sup>9</sup> Recently, the electronic absorption spectra of  $B_3$  and  $B_3^-$  in Ne matrix,<sup>29</sup> and the gas phase photoelectron spectra<sup>30</sup> of  $B_3^-$  and  $B_4^-$  were reported.

The present work deals with the *ab initio* calculations of the low lying vibrational levels in the most stable rhombic  $B_4$  isomer in its  $X^1A_g$  ground state. In previous theoretical studies<sup>10–12,22–28,30</sup> the equilibrium structures<sup>11,12,22–25,28,30</sup> and harmonic wave numbers<sup>25,26,30</sup> were calculated for the  $D_{2h}$  rhombic minimum or for the square  $D_{4h}$  transition state. However, the computations of a realistic pattern of vibrational levels in  $B_4$  require methods going beyond the harmonic approximation. The existence of two equivalent minima (there are six equivalent ones if permutations including bond breaking are considered to be feasible symmetry operations) leads to splittings and additional complications for the vibrational assignments are caused by the presence of strong low lying anharmonic resonances.

In the tetraatomic cyclic clusters, the lower symmetry minima can correlate with electronically degenerate states of higher symmetry forming Jahn–Teller pairs. In fact, the theory for this type of Born–Oppenheimer breakdown has

been originally formulated for the  $X_4$  planar molecules.<sup>31,32</sup> Based on the model of Pearson,<sup>33</sup> the planar rhombic equilibrium structures have been considered in previous theoretical studies (for instance, in Ref. 25) as a result of the second-order (pseudo) Jahn–Teller effect. The coupling of at least two electronic states is supposed to lead to the  $D_{2h}$  rhomboid minimum. The archetypical example<sup>33</sup> of the pseudo-Jahn–Teller effect is the ammonia-like  $D_{3h}/C_{3v}$  structure, in which the ground and the first excited singlet states are coupled by the inversion mode. Recent calculations clearly showed that the near-equilibrium vibrational problem can be solved very accurately within the Born–Oppenheimer approximation.<sup>34–36</sup> In  $B_4$  the coupling is via the  $B_{1g}$  mode, which distorts the square molecule to its planar rhombic  $X^1A_g$  form. Like in ammonia, the first electronically excited singlet state in  $B_4$  is energetically well separated from the ground state. We have calculated the vertical excitation energy to the  $A^1B_{1g}$  state at 3.1 eV above the rhombic equilibrium and 3.3 eV above the square barrier (cf. following section). In the photodetachment electron spectra of  $B_4^-$  (Ref. 30) only excited triplet states were detected, lying between 1 and 2.4 eV above the  $X^1A_g$  ground state. The excited singlet states were calculated at higher energies.<sup>30</sup> On the electronic ground state potential energy surface (PES) the next higher isomer having  $C_{2v}$  symmetry has been calculated to lie at 1.77 eV,<sup>11</sup> or 2.33 eV<sup>12</sup> with a barrier on the isomerization path of 0.43 eV<sup>12</sup> above the rhombic structure. Therefore, for the energy region of the fundamental vibrational transitions a single adiabatic PES with two equivalent minima is consid-

TABLE I. Definition of the symmetry relations of the planar structures used in the assignments.

Mode	$D_{4h}$ $^{10}B_4, ^{11}B_4$	$D_{2h}^a$ $^{10}B_2, ^{11}B_2$	$C_{2v}^b$ $^{10}B^{11}B_3, ^{11}B^{10}B_3$	$C_{2v}^b$ $^{10}B_2, ^{11}B_2$	$C_s$
1	$A_{1g}$	$A_g$	$A_1$	$A_1$	$A'$
2	$B_{1g}$	$A_g$	$A_1$	$B_2$	$A'$
3	$B_{2g}$	$B_{1g}$	$B_2$	$A_1$	$A'$
4	$B_{2u}$	$B_{1u}$	$B_1$	$A_2$	$A''$
5	$E_u$	$B_{2u} + B_{3u}$	$A_1 + B_2$	$A_1 + B_2$	$2A'$

<sup>a</sup> $z$  axis is perpendicular to the  $\sigma(xy)$  molecular plane.

<sup>b</sup> $C_2$  lies in the  $z$  axis and  $\sigma(yz)$  is the molecular plane.

ered to be a sufficiently good approximation.

Similar rhombus/square PES topology has been predicted in electronic ground and excited states of numerous  $X_4$  clusters, for instance, in  $Li_4$ ,<sup>37,38</sup>  $C_4$ ,<sup>39</sup> or  $Au_4$ .<sup>40,41</sup> Interestingly, in  $Si_3C$  two distinct rhombic planar structures were detected experimentally<sup>42</sup> and one of the isomers in interstellar space.<sup>42</sup>

The nuclear motion problem has been solved by the MULTIMODE approach.<sup>43</sup> It has been demonstrated that MULTIMODE can deliver a near-exact set of vibrational energies for molecules such as ammonia,<sup>44</sup> where tunneling through a potential barrier is experienced. Using the same PES, identical variational results were obtained with MULTIMODE with the full Hamiltonian in internal coordinates<sup>45</sup> and with the reaction path Hamiltonian.<sup>46</sup> The MULTIMODE method requires a stationary point at which a normal mode analysis is performed. The obvious choice for ammonia, where tunneling splittings were of interest, was the inversion saddle point of  $D_{3h}$  symmetry. Similarly, for  $B_4$ , the square  $D_{4h}$  saddle point is used to obtain the normal modes required for the variational calculations of the anharmonic wave functions.

## II. COMPUTATIONAL APPROACH

All electronic structure calculations were carried out using the MOLPRO program.<sup>47</sup> The valence electronic configuration of the  $B_4$  electronic ground state  $X^1A_g(D_{2h})$  is  $1a_g^2 1b_{2u}^2 1b_{3u}^2 1b_{1u}^2 1b_2^2 2a_g^2$ . Because it dominates the configuration expansion in the region near the  $D_{4h}$  barrier and at the minimum  $D_{2h}$  structure, we used the coupled cluster with perturbative triples (CCSD(T)) method<sup>48</sup> and the correlation-consistent polarized valence quadruple zeta basis set (cc-pVQZ) of Dunning<sup>49</sup> to calculate the 643 energies used in the analytical fit. The core and core-valence electron correlation was neglected. The vertical excitation energy of the first electronically excited  $A^1B_{1g}$  state at the optimized rhombic equilibrium structure (cf. following section) has been calculated to be 3.12 eV equation of motion-coupled clusters (EOM-CC);<sup>50</sup> cc-pVQZ basis set<sup>49</sup> and 2.92 eV full valence complete active space self-consistent field (CASSCF),<sup>51</sup> aug-cc-pVTZ basis set<sup>49</sup>, for the square structure 3.35 eV (EOM-CC) and 3.82 eV (full valence CASSCF). As we have performed calculations for all six stable isotopomers of  $B_4$  we define for clarity the symmetry relations between different point groups used. In Table I the definition of axis, planes, and corresponding irreducible representations are given. After having tested various types of

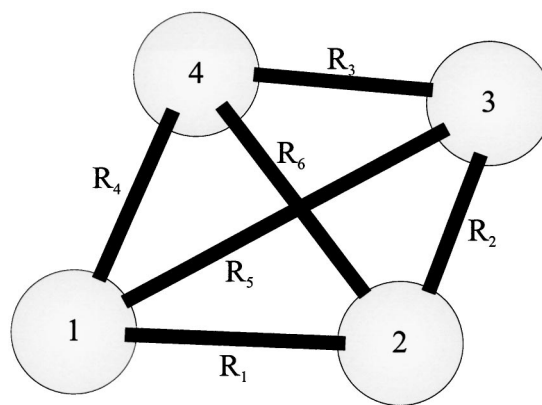


FIG. 1. Nuclear distances employed in the definition of the symmetry coordinates.

coordinates the best six-dimensional fit was obtained with the following  $D_{2h}$  symmetry-adapted coordinates (see Fig. 1 for the definition of the distances):

$$S_{1A_g} = \frac{1}{2}(\Delta R_1 + \Delta R_2 + \Delta R_3 + \Delta R_4),$$

$$S_{2B_{1g}} = \frac{1}{2}(\Delta R_1 - \Delta R_2 + \Delta R_3 - \Delta R_4),$$

$$S_{3B_{2u}} = \frac{1}{2}(\Delta R_1 - \Delta R_2 - \Delta R_3 + \Delta R_4),$$

$$S_{4B_{3u}} = \frac{1}{2}(\Delta R_1 + \Delta R_2 - \Delta R_3 - \Delta R_4),$$

$$S_{5A_g} = \frac{1}{\sqrt{2}}(\Delta R_5 - \Delta R_6),$$

$$S_{6B_{1u}} = \Delta \tau,$$

$\tau$  being the dihedral angle between the planes  $B_1-B_2-B_3$  and  $B_2-B_3-B_4$ . The following polynomial expansion is used to represent the six-dimensional double minimum PES:

$$V(S_1, S_2, \dots, S_6) = \sum_{i,j,k,l,m,n=0}^4 C_{i,j,k,l,m,n} S_1^i S_2^j S_3^k S_4^l S_5^m S_6^n.$$

In the expansion only the totally symmetric products with  $i+j+k+l+m \leq 4$  were retained. In the planar square reference geometry  $R_i^0 = 2.8986$  bohrs ( $i=1,4$ ),  $R_j^0 = 2.8986 \times \sqrt{2}$  bohr ( $j=5,6$ ), and  $\tau^0 = 0$ . The following relation including permutations of the coordinates holds:  $V(S_1, S_2, S_3, S_4, S_5, S_6) = V(S_1, S_2, -S_4, -S_3, -S_5, -S_6)$ . The goal was to obtain a PES valid close to the minimum and the barrier. The analytic form of the double minimum PES is available from the data base.<sup>52</sup>

In Fig. 2 contour plots are displayed for some typical cuts of the PES. The units on the axis are bohr for the distances and degree for the  $S_6$  coordinate. For a given pair of coordinates all the others are fixed at the optimized geometry of the square transition state (cf. Table II). The two-dimensional cut of the  $S_4$  versus  $S_3$  coordinates shows an isotropic form. In fact, due to the totally symmetric products in the expansion and the aforementioned symmetry relation, the cut must be symmetric with respect to  $S_3 = -S_4$  and  $S_3 = S_4$  coordinate permutations. The second cut,  $S_6$  versus  $S_1$ ,

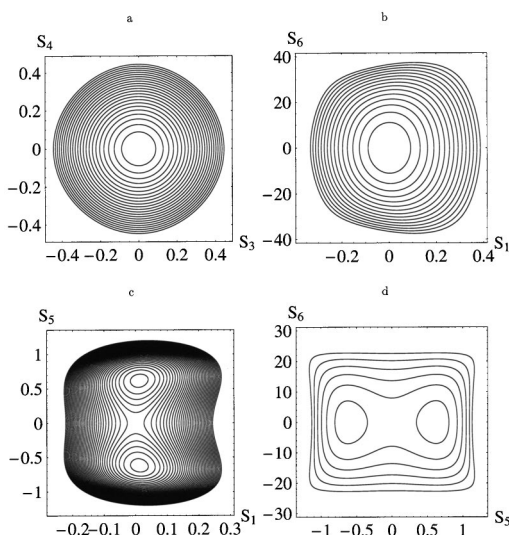


FIG. 2. Four contour plots of the double minimum six-dimensional PES of the  $B_4$  rhombic cluster in symmetry coordinates. The distance is in bohr and angle in degree. Contour a: energy range  $6000\text{ cm}^{-1}$ , contour step  $250\text{ cm}^{-1}$ . Contour b: energy range  $4000\text{ cm}^{-1}$ , contour step  $250\text{ cm}^{-1}$ . Contour c: energy range  $2000\text{ cm}^{-1}$ , contour step  $50\text{ cm}^{-1}$ . Contour d: energy range  $1750\text{ cm}^{-1}$ , contour step  $250\text{ cm}^{-1}$ .

displays the potential for all in-plane ( $S_6=0$ ) and out-of-plane ( $S_6\neq 0$ ) geometries, in which  $R_1=R_2=R_3=R_4$  and  $R_5=R_6$ . The  $S_5$  versus  $S_1$  cut, including the rhombic minima, gives information on how the equal sides of the tetragon ( $S_2=S_3=S_4=0$ ) become larger when passing from the square to the rhombic structure (the  $S_1$  value is positive for the rhombic minimum and zero for the square structure). The  $S_6$  versus  $S_5$  cut in the last diagram shows the change of the energy barrier with increasing out-of-plane angle, for squeezing a tetragon with  $R_1=R_2=R_3=R_4=R_i^0$ .

The barrier height (on the adiabatic PES) relative to the rhombic minimum has been calculated to be  $255\text{ cm}^{-1}$ . Previously Martin *et al.*<sup>25</sup> reported  $178\text{ cm}^{-1}$  ( $G1$  corrected value), Zhai *et al.*<sup>30</sup>  $283\text{ cm}^{-1}$  (B3LYP), and Kato and Tanaka<sup>26</sup>  $1014\text{ cm}^{-1}$  (MP4).

The analysis of the PES indicates that the path corresponding to two clockwise and two anticlockwise in-phase nuclear in-plane rotations for the  $r\cos(\theta)$  coordinate with  $r=(d_1-d_2)/4$ , and  $d_1$  being the long and  $d_2$  the short diagonal of the rhombus, represents a good approximation for the periodic  $B_{1g}$  ring distortion. However, there is no path connecting the two rhombic minima below the square transition state.

The PES described above was used in vibrational variational calculations with the code MULTIMODE.<sup>53</sup> This procedure utilizes the exact Watson kinetic energy operator in normal coordinates,<sup>54</sup> and therefore some suitable reference structure at which the  $3N-6$  normal vibrations are defined must be first located. In order to be even handed about the two equivalent minima on the PES, the choice for such a reference structure is that of the square-planar transition state. The normal mode vectors at the transition state can then be readily specified in terms of the irreducible representations of the symmetry point group for any chosen isotopomer. However, due to the specific difficulties in employing  $C_{2v}$  symmetry (the highest currently available in MULTIMODE) for molecules with  $E$  modes in the  $D_{4h}$  point group, all we can do is to use the reflection operation in order to symmetry block the configuration interaction (CI) matrix; we therefore work in  $C_s$  symmetry throughout (two blocks  $A'$  and  $A''$ ), and use the vector symmetries in order to reclassify the energy levels into irreducible representations of the point group of the transition state. The great advantage of the MULTIMODE approach in the application to the  $B_4$  problem is the possibility to designate the anharmonic vibrational states in terms of linear combinations of vibrational configurations with harmonic quantum numbers. This is a universal bonus gained from using normal coordinates and has been the method of choice for spectroscopists for many years.

The methodology adopted in the MULTIMODE approach has been fully described on a number of occasions (see Ref. 53 and references therein). We therefore only outline the basic features relevant to this work. The initial step in the procedure is to optimize a set of 36 harmonic-oscillator primi-

TABLE II. Optimized geometries (diagonal distances) and the harmonic wave numbers of the fundamental vibrational transition in the electronic ground states of  $B_4$ .

		$B_4$ rhombus ( $D_{2h}$ )			$B_4$ square ( $D_{4h}$ )		
		This work <sup>a</sup>	b	c	This work <sup>a</sup>	b	
Diagonals (bohr)		4.591	4.703	4.659	4.100	4.126	
		3.574	3.520	3.601			
Modes ( $\text{cm}^{-1}$ )	$\omega_1$	$A_g$	1142	1118	$A_{1g}$	1143	1136
	$\omega_2$	$A_g$	311	433	$B_{1g}$	209i	330i
	$\omega_3$	$B_{1g}$	1216	1161	$B_{2g}$	1240	1195
	$\omega_4$	$B_{1u}$	304	332	$B_{2u}$	272	238
	$\omega_5$	$B_{2u}$	1013	970	$E_u$	1148	1138
	$\omega_5$	$B_{3u}$	1235	1251	$E_u$	1148	1138

<sup>a</sup>The harmonic wave numbers were calculated with the relative atomic mass of 10.810 for boron; cc-pVQZ basis was used (Ref. 49), the CCSD(T) total energies at the rhombic and square structures were calculated to be  $-98.908\,391\text{ a.u.}$  and  $-98.907\,260\text{ a.u.}$  The standard MOLPRO convergency criteria for the gradients and energies were used.

<sup>b</sup>MP2 approach/6-311G\*; no relative mass of  $B$  was given (Ref. 25).

<sup>c</sup>RCCSD(T)/6-311+G\*,  $E_{\min}=-98.839\,444\text{ a.u.}$ ; no relative mass of  $B$  was given (Ref. 30).

tive basis functions (NBF) for  $3N-7$  normal modes by using effective one-dimensional cuts in the PES relative to the “squeezing” mode. These one-dimensional potentials are then used in variational calculations with the equivalent one-dimensional Hamiltonians, respectively, for which ten converged subsets (NVF) are retained for subsequent use. The raw one-dimensional, double-minimum cut is used for the squeezing mode itself (NBF=46, NVF=15), in order to optimize the corresponding harmonic-oscillator basis. The primitive harmonic-oscillator basis is defined by the values of  $\omega$  arising from the Wilson FG normal mode analysis, with the exception of that for the squeezing mode, whose eigenvalue is imaginary at the planar transition state. In this case pilot calculations are carried out with various values of  $\omega$  assigned to the harmonic-oscillator basis, until an optimum value is obtained which spans sufficiently into the high-energy regions of the one-dimensional cut. Providing that a sufficient number of primitive harmonic-oscillator functions are used, fully converged one-dimensional expansion functions can be obtained for modes with such gross anharmonicity. This optimization procedure is carried out using Gauss-hermite numerical quadrature involving quadrature points to integrate all matrix elements (50 for the  $3N-7$  normal modes and 60 for the squeezing mode), and the resulting contracted expansion functions are then used to reduce the integration points via the HEG algorithm.<sup>55</sup>

The optimized one-dimensional expansion set is now used in a vibrational self-consistent-field procedure for the zero-point level. Integration of the matrix elements takes place in a series of steps ( $\leq 5$ ), during which the overcounting of each  $M$ -mode potential resulting from  $M+1$ -mode cuts (and so on) is taken into account.<sup>43</sup> Likewise, integration of the Coriolis terms which involve the inverse moment-of-inertia tensor  $\mu$  is performed in an analogous way. For each  $M$ -mode cut in the PES and  $\mu$ , the equivalent  $M$ -mode Hamiltonian is adopted. The result of this analysis is an improved one-dimensional expansion set in the NVF basis for each of the  $3N-6$  modes, and these are now used in a final CI calculation to determine the vibrational energies. The CI matrix itself is constructed by imposing a maximum quantum for each mode, together with a maximum sum-over-quanta for all modes, in a series of  $M$ -mode blocks ( $M \leq 5$ ). The complete CI matrix is the total of all such blocks.<sup>53</sup> Finally, the resulting CI matrix is split into  $A'$  and  $A''$  symmetry blocks. As with all variational calculations, increased CI matrices are diagonalized until the required convergence is reached. In MULTIMODE calculations, a further convergence criterion is required, and that is for the  $M$ -mode integration procedure. In this study, virtually total convergence in all levels was achieved for  $M=5$ , and this therefore removes the inherent approximation from the calculations.

### III. RESULTS AND DISCUSSION

The computational approach used for the generation of the six-dimensional PES yielded the following spectroscopic constants for the  $^{11}\text{B}_2 X^3\Sigma_g^-$  state:  $R_e=1.593 \text{ \AA}$ ,  $\omega_e=1048 \text{ cm}^{-1}$ , and  $\omega_e x_e=8.92 \text{ cm}^{-1}$ . The corresponding ex-

perimental values<sup>8</sup> are  $R_e=1.590 \text{ \AA}$ ,  $\omega_e=1051.3 \text{ cm}^{-1}$ , and  $\omega_e x_e=9.35 \text{ cm}^{-1}$ . It is difficult to estimate the accuracy of the fundamental transitions evaluated from the six-dimensional PES of  $B_4$ , but we expect to have obtained similarly reliable results. The CCSD(T) geometries and harmonic wave numbers for the minimum and the saddle point of  $B_4$  are compared with previous theoretical data in Table II. The similarity of the  $B-B$  equilibrium distances in  $B_2$  and  $B_4$  is related to the covalent character of the bonds in the cluster. For  $D_{4h}$  structures only one imaginary wave number is calculated for the  $B_{1g}$  mode, which transforms the square transition state to the rhombic minimum. Our optimized diagonal distances and harmonic wave numbers for  $B_4$  differ from those calculated previously. The present results are seen to be more accurate due to the better quality of the electronic structure calculations.

The CCSD(T) values for the  $\omega_2$  ring in-plane distortion and the  $\omega_4$  ring out-of-plane bending are calculated to be almost identical. This implies that overtones or combination levels with even vibrational quanta will form anharmonic resonances considerably complicating the splitting patterns and assignments. Within a given symmetry block other nearby states interact as well.

In nature there are two stable boron isotopes,  $^{10}\text{B}$  (abundance 19.9%) and  $^{11}\text{B}$  (80.1%), which give rise to six different isotopomers of  $B_4$  belonging to different point groups. The MULTIMODE calculations were all done using  $C_s$  symmetry with the plane in which the four boron atoms lie at the transition state, defining the symmetry plane. In all six isotopomers the vibrational states in Table III are assigned with the highest possible symmetries of the transition states. In the first column the consecutive numbering of all levels is used and the labels  $l$  (lower) and  $u$  (upper) indicate the split pairs. In the second column the harmonic vibrational configurations (with coefficients larger than 0.3 in the configuration expansion) are given for  $^{11}\text{B}_4$ . The mode numbering is defined in Table I. The results are presented in two blocks—Table III for  $A'$  symmetry and Table IV for  $A''$  symmetry. All calculated levels for  $^{11}\text{B}_4$  up to about  $1500 \text{ cm}^{-1}$  are displayed in Fig. 3, with assignments using the irreducible representations of the  $D_{4h}$  point group. Each state is designated by specifying the dominating harmonic configurations in the total wave function expansion. The zero-point energies are given relative to the electronic energy of the transition state and vary up to  $122 \text{ cm}^{-1}$  for different isotopomers. The vibrational mode splittings were deduced from the assignments in Tables III and IV. The anharmonic fundamental vibrational levels of  $^{11}\text{B}_4$  are calculated to be (splittings in parentheses):  $G(0)=2352(22) \text{ cm}^{-1}$ ,  $\nu_1(A_{1g})=1136(24) \text{ cm}^{-1}$ ,  $\nu_2(B_{1g})=209(144) \text{ cm}^{-1}$ ,  $\nu_3(B_{2g})=1198(19) \text{ cm}^{-1}$ ,  $\nu_4(B_{2u})=271(24) \text{ cm}^{-1}$ , and  $\nu_5(E_u)=1030(166) \text{ cm}^{-1}$ . The corresponding values for the second abundant  $^{10}\text{B}^{11}\text{B}_3$  isotopomer are 2364 (23), 1148 (24), 212 (148), 1218 (21), 274 (25), and 1041, 1042 (158,160) (all values in  $\text{cm}^{-1}$ ). All IR or Raman allowed fundamentals of these two isotopomers will be clearly discernible in their spectra. According to the splittings in the ground state of about  $22\text{--}26 \text{ cm}^{-1}$  the rhombus will rearrange within about  $0.75 \text{ ps}$ , and at room temperature, because the  $B_{1g}$  and

TABLE III. Vibrational pattern in the  $B_4$  isotopomers ( $A'$  symmetry).

Abundance (%)		$^{11}B_4$ 41.2		$^{10}B^{11}B_3$ 40.9		$^{10}B_2^{11}B_2$ 10.2		$^{10}B_2^{11}B_2$ 5.1		$^{10}B_3^{11}B$ 2.5		$^{10}B_4$ 0.2	
Assignment <sup>a</sup>		$D_{4h}$		$C_{2v}$		$C_{2v}$		$D_{2h}$		$C_{2v}$		$D_{4h}$	
$0^l$	$G(0)$	$A_{1g}$	2332.76	$A_1$	2363.60	$A_1$	2394.13	$A_g$	2394.36	$A_1$	2424.58	$A_{1g}$	2454.73
$0^u$	$2^1$	$B_{1g}$	21.89	$A_1$	22.97	$B_2$	24.03	$A_g$	24.12	$A_1$	25.18	$B_{1g}$	26.32
$1^l$	$2^2$	$A_{1g}$	209.15	$A_1$	212.07	$A_1$	215.12	$A_g$	215.02	$A_1$	218.21	$A_{1g}$	221.46
$1^u$	$2^3$	$B_{1g}$	353.36	$A_1$	359.70	$B_2$	366.30	$A_g$	366.04	$A_1$	372.91	$B_{1g}$	379.81
$2^l$	$4^2+2^4$	$A_{1g}$	534.62	$A_1$	541.69	$A_1$	548.57	$A_g$	548.48	$A_1$	555.21	$A_{1g}$	561.76
$2^l$	$2^4+4^2$	$A_{1g}$	556.36	$A_1$	565.28	$A_1$	574.68	$A_g$	574.33	$A_1$	584.23	$A_{1g}$	594.27
$2^u$	$2^14^2$	$B_{1g}$	566.79	$A_1$	574.14	$B_2$	581.37	$A_g$	581.52	$A_1$	588.60	$B_{1g}$	595.82
$3^l$	$2^24^2$	$A_{1g}$	724.64	$A_1$	733.43	$A_1$	742.22	$A_g$	742.18	$A_1$	750.99	$A_{1g}$	759.88
$2^u$	$2^5$	$B_{1g}$	765.29	$A_1$	778.55	$B_2$	792.32	$A_g$	791.72	$A_1$	806.02	$B_{1g}$	820.25
$3^u$	$2^34^2$	$B_{1g}$	860.94	$A_1$	872.57	$B_2$	884.35	$A_g$	884.17	$A_1$	896.09	$B_{1g}$	908.12
$4^l$	$2^6+2^44^2$	$A_{1g}$	988.01	$A_1$	1002.77	$A_1$	1017.65	$A_g$	1017.13	$A_1$	1032.12	$A_{1g}$	1046.72
$5^l$	$5^1+2^15^1$	$E_u$	1030.05	$A_1$	1041.37	$A_1$	1053.05	$B_{2u}$	1054.31	$A_1$	1064.36	$E_u$	1080.72
$5^l$	$5^1+2^15^1$	$E_u$	1030.11	$B_2$	1042.35	$B_2$	1054.11	$B_{3u}$	1057.15	$B_2$	1068.28	$E_u$	1080.81
$4^l$	$2^44^2+2^6+4^4$	$A_{1g}$	1036.31	$A_1$	1052.02	$A_1$	1068.21	$A_g$	1067.52	$A_1$	1084.36	$A_{1g}$	1101.17
$4^l$	$4^4+2^44^2$	$A_{1g}$	1094.36	$A_1$	1107.79	$A_1$	1121.15	$A_g$	1120.98	$A_1$	1134.45	$A_{1g}$	1147.90
$4^u$	$2^14^4$	$B_{1g}$	1102.23	$A_1$	1115.63	$B_2$	1128.67	$A_g$	1128.85	$A_1$	1141.72	$B_{1g}$	1154.72
$6^l$	$1^1$	$A_{1g}$	1135.76	$A_1$	1148.43	$A_1$	1161.16	$A_g$	1163.19	$A_1$	1175.44	$A_{1g}$	1190.15
$6^u$	$2^11^1$	$B_{1g}$	1159.79	$A_1$	1172.51	$B_2$	1184.79	$A_g$	1189.93	$A_1$	1202.63	$B_{1g}$	1218.94
$5^u$	$5^1+2^15^1$	$E_u$	1196.03	$A_1$	1199.80	$A_1$	1213.39	$B_{3u}$	1223.80	$B_2$	1227.26	$E_u$	1252.36
$5^u$	$2^15^1+5^1$	$E_u$	1196.08	$B_2$	1214.26	$B_2$	1222.48	$B_{2u}$	1225.18	$A_1$	1242.74	$E_u$	1252.41
$7^l$	$3^1$	$B_{2g}$	1198.45	$B_2$	1218.12	$A_1$	1242.11	$B_{1g}$	1225.75	$B_2$	1249.36	$B_{2g}$	1255.58
$4^u$	$2^54^2+2^7+2^14^4$	$B_{1g}$	1206.48	$A_1$	1223.05	$B_2$	1239.72	$A_g$	1239.24	$A_1$	1256.19	$B_{1g}$	1272.89
$7^u$	$2^13^1$	$A_{2g}$	1217.94	$B_2$	1239.47	$B_2$	1255.99	$B_{1g}$	1250.60	$B_2$	1267.22	$A_{2g}$	1279.17
$8^l$	$2^24^4$	$A_{1g}$	1239.17	$A_1$	1253.93	$A_1$	1268.42	$A_g$	1268.36	$A_1$	1282.89	$A_{1g}$	1297.43
$4^u$	$2^7+2^54^2$	$B_{1g}$	1282.67	$A_1$	1303.99	$B_2$	1326.08	$A_g$	1325.64	$A_1$	1347.35	$B_{1g}$	1372.28
$9^l$	$2^25^1$	$E_u$	1302.35	$B_2$	1316.58	$A_1$	1327.45	$B_{2u}$	1333.96	$A_1$	1349.56	$E_u$	1367.28
$9^l$	$2^25^1$	$E_u$	1302.60	$A_1$	1317.14	$B_2$	1336.11	$B_{3u}$	1336.05	$B_2$	1350.94	$E_u$	1367.62
$10^l$	$2^21^1$	$A_{1g}$	1344.13	$A_1$	1363.58	$A_1$	1382.20	$A_g$	1377.86	$A_1$	1397.03	$A_{1g}$	1411.39
$8^u$	$2^34^4+2^54^2$	$B_{1g}$	1378.39	$A_1$	1396.31	$B_2$	1414.12	$A_g$	1413.88	$A_1$	1431.98	$B_{1g}$	1450.08
$11^l$	$2^24^2$	$A_{1g}$	1405.12	$A_1$	1423.42	$A_1$	1441.83	$A_g$	1441.19	$A_1$	1459.89	$A_{1g}$	1478.86
$12^l$	$2^23^1$	$B_{2g}$	1408.77	$B_2$	1426.58	$A_1$	1444.26	$B_{1g}$	1443.22	$B_2$	1460.98	$B_{2g}$	1477.24
$9^u$	$2^35^1$	$E_u$	1464.38	$B_2$	1480.50	$B_2$	1493.83	$B_{2u}$	1502.51	$A_1$	1518.89	$E_u$	1541.77
$9^u$	$2^35^1$	$E_u$	1464.59	$A_1$	1482.65	$A_1$	1505.27	$B_{3u}$	1503.46	$B_2$	1521.99	$E_u$	1542.01
$10^u$	$2^31^1$	$B_{1g}$	1492.89	$A_1$	1516.85	$B_2$	1539.38	$A_g$	1533.56	$A_1$	1557.49	$B_{1g}$	1574.50
$13^l$	$2^3+2^44^4$	$A_{1g}$	1529.39	$A_1$	1551.44	$A_1$	1573.32	$A_g$	1572.68	$A_1$	1594.87	$A_{1g}$	1616.48
$12^u$	$2^33^1$	$A_{2g}$	1548.39	$B_2$	1570.28	$B_2$	1591.98	$B_{1g}$	1589.64	$B_2$	1611.41	$A_{2g}$	1631.25
$13^l$	$2^3+2^64^2+2^44^4$	$A_{1g}$	1567.62	$A_1$	1592.47	$A_1$	1619.08	$A_g$	1618.13	$A_1$	1645.58	$A_{1g}$	1673.27
$14^l$	$4^25^1+2^14^25^1$	$E_u$	1574.33	$A_1$	1591.47	$A_1$	1609.47	$B_{2u}$	1610.52	$A_1$	1629.39	$E_u$	1649.15
$14^l$	$4^25^1+2^14^25^1$	$E_u$	1574.85	$B_2$	1594.93	$B_2$	1611.28	$B_{3u}$	1614.34	$B_2$	1631.45	$E_u$	1649.69

<sup>a</sup>The first column lists pairs of levels split by the  $B_{1g}$  ( $D_{4h}$ ) motion. The  $l$  and  $u$  labels designate lower and upper levels, respectively. The vibrational quantum numbers of the  $b_{1g}$  distortion mode in the  $u$  and  $l$  vibrational configurations differ by one. The pairs are numbered according to increasing wave numbers. When two levels correspond to the same combination of vibrational configurations, they are attributed to the same pair. Second column gives the leading harmonic vibrational configurations of the wave function.

$B_{2u}$  fundamentals will also be populated, the cycle will undergo a complex motion including the out-of-plane bending.

The term pattern is complicated by the presence of strong anharmonic resonances. In the  $A'$  block, for instance, the harmonic states with two quanta in the  $B_{1g}$  distortion and two quanta in the out-of-plane  $B_{2u}$  form a lower ( $2^l$  in Table III) anharmonic pair at 535 and 556  $\text{cm}^{-1}$  in  $^{11}B_4$ , their upper counterparts ( $2^u$ ) are calculated to lie at 567 and 765  $\text{cm}^{-1}$ . In the  $A''$  block the  $3^l$  pair lies at 780 and 823  $\text{cm}^{-1}$ , the  $3^u$  pair at 836 and 992  $\text{cm}^{-1}$ . The assignments of the split states becomes difficult going up the ladder and the attribution to the upper and lower levels in Tables III and IV are only tentative. Similar resonances exist also in other isotopomers. The calculations yield essentially identical vibrational energies for the two possible  $C_{2v}$  rhombic isotopomers

$^{10}B_2^{11}B_2$ , but the anharmonic couplings lead to shifts particularly in the region of the  $E$  modes.

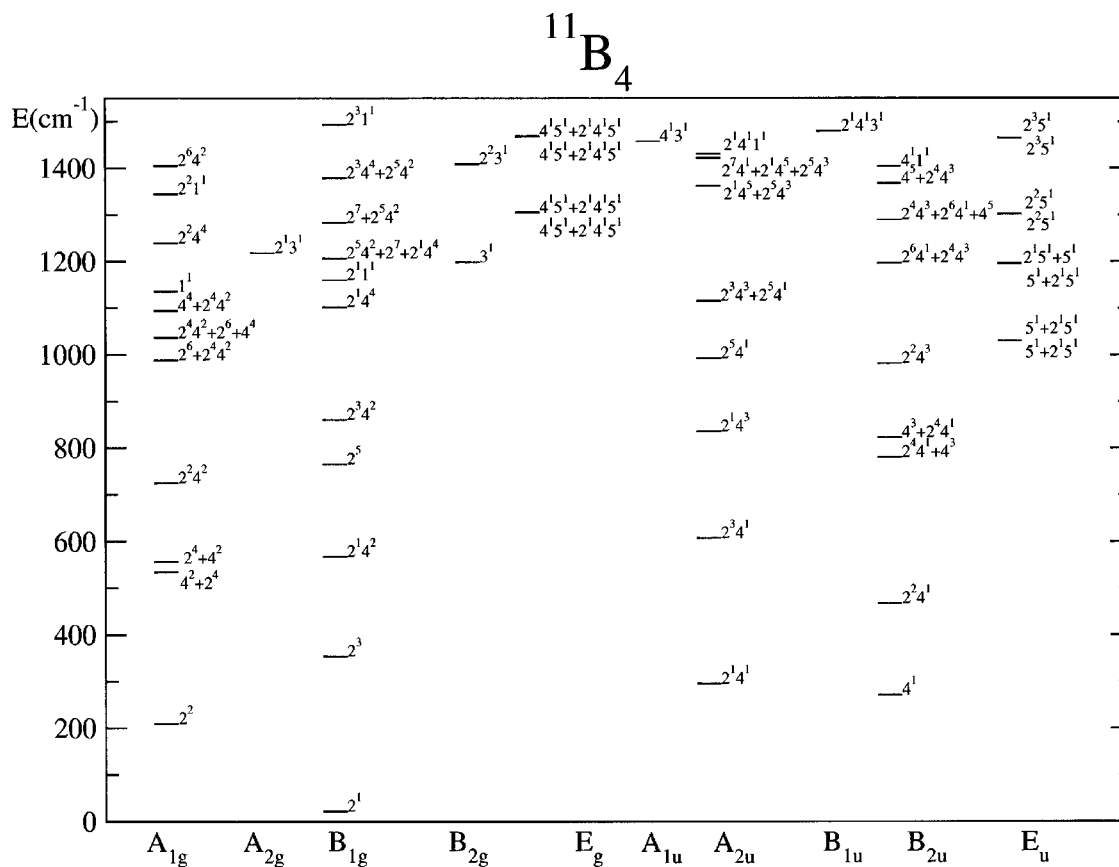
#### IV. SUMMARY AND CONCLUSION

To date, only the photodetachment spectrum of rhombic  $B_4^-$  has yielded experimental information on the ground state of  $B_4$ . The detected band is broad with no distinguishable vibrational progression.<sup>30</sup>

In the present work we used a double minimum six-dimensional CCSD(T) PES for the lowest isomer of  $B_4$  to solve the anharmonic nuclear motion problem by the MULTIMODE approach. The calculated splittings of the fundamental levels (around 20  $\text{cm}^{-1}$ ) indicate that the rhombic structure rearranges on the time scale of about 0.75 ps. The presence of the splittings, anharmonic resonances, hot bands, and

TABLE IV. Vibrational pattern in the  $B_4$  isotopomers ( $A''$  symmetry).

Abundance (%)		$^{11}B_4$ 41.2		$^{10}B^{11}B_3$ 40.9		$^{10}B_2^{11}B_2$ 10.2		$^{10}B_2^{11}B_2$ 5.1		$^{10}B_3^{11}B$ 2.5		$^{10}B_4$ 0.2	
Assignment <sup>a</sup>		$D_{4h}$		$C_{2v}$		$C_{2v}$		$D_{2h}$		$C_{2v}$		$D_{4h}$	
$1^l$	$4^1$	$B_{2u}$	271.28	$B_1$	274.43	$A_2$	277.53	$B_{1u}$	277.53	$B_1$	280.58	$B_{2u}$	283.62
$1^u$	$2^1 4^1$	$A_{2u}$	295.18	$B_1$	299.42	$B_1$	303.61	$B_{1u}$	303.72	$B_1$	307.84	$A_{2u}$	312.05
$2^l$	$2^2 4^1$	$B_{2u}$	467.28	$B_1$	473.17	$A_2$	479.13	$B_{1u}$	479.06	$B_1$	485.11	$B_{2u}$	491.22
$2^u$	$2^3 4^1$	$A_{2u}$	607.22	$B_1$	616.13	$B_1$	625.21	$B_{1u}$	625.02	$B_1$	634.27	$A_{2u}$	643.60
$3^l$	$2^4 4^1 + 4^3$	$B_{2u}$	780.37	$B_1$	791.07	$A_2$	801.78	$B_{1u}$	801.55	$B_1$	812.29	$B_{2u}$	822.90
$3^l$	$4^3 + 2^4 4^1$	$B_{2u}$	822.86	$B_1$	833.33	$A_2$	843.89	$B_{1u}$	843.76	$B_1$	854.47	$B_{2u}$	865.25
$3^u$	$2^1 4^3$	$A_{2u}$	835.88	$B_1$	846.24	$B_1$	856.40	$B_{1u}$	856.56	$B_1$	866.54	$A_{2u}$	876.64
$4^l$	$2^2 4^3$	$B_{2u}$	981.52	$B_1$	993.24	$A_2$	1004.87	$B_{1u}$	1004.77	$B_1$	1016.40	$B_{2u}$	1028.04
$3^u$	$2^5 4^1$	$A_{2u}$	992.46	$B_1$	1006.94	$B_1$	1021.72	$B_{1u}$	1021.29	$B_1$	1036.35	$A_{2u}$	1051.39
$4^u$	$2^3 4^3 + 2^5 4^1$	$A_{2u}$	1115.54	$B_1$	1130.13	$B_1$	1144.74	$B_{1u}$	1144.47	$B_1$	1159.28	$A_{2u}$	1174.07
$5^l$	$2^6 4^1 + 2^4 4^3$	$B_{2u}$	1197.32	$B_1$	1213.67	$A_2$	1230.10	$B_{1u}$	1229.56	$B_1$	1246.27	$B_{2u}$	1262.71
$5^l$	$2^4 4^3 + 2^6 4^1 + 4^5$	$B_{2u}$	1289.36	$B_1$	1307.33	$A_2$	1325.39	$B_{1u}$	1325.11	$B_1$	1343.75	$B_{2u}$	1362.26
$6^l$	$4^1 5^1 + 2^1 4^1 5^1$	$E_g$	1304.69	$B_1$	1318.96	$B_1$	1334.22	$B_{2g}$	1335.00	$B_1$	1351.02	$E_g$	1367.67
$6^l$	$4^1 5^1 + 2^1 4^1 5^1$	$E_g$	1304.92	$A_2$	1321.52	$A_2$	1335.22	$B_{3g}$	1338.43	$A_2$	1352.50	$E_g$	1368.00
$5^u$	$2^1 4^5 + 2^5 4^3$	$A_{2u}$	1361.90	$B_1$	1379.49	$B_1$	1395.76	$B_{1u}$	1394.47	$B_1$	1411.52	$A_{2u}$	1426.89
$7^l$	$4^5 + 2^4 4^3$	$B_{2u}$	1367.46	$B_1$	1384.22	$A_2$	1400.32	$B_{1u}$	1400.21	$B_1$	1416.46	$B_{2u}$	1432.42
$8^l$	$4^1 1^1$	$B_{2u}$	1404.14	$B_1$	1419.99	$A_2$	1436.04	$B_{1u}$	1437.81	$B_1$	1453.30	$B_{2u}$	1470.65
$7^u$	$2^7 4^1 + 2^1 4^5 + 2^5 4^3$	$A_{2u}$	1422.01	$B_1$	1441.26	$B_1$	1459.93	$B_{1u}$	1459.21	$B_1$	1478.49	$A_{2u}$	1496.97
$8^u$	$2^1 4^1 1^1$	$A_{2u}$	1430.78	$B_1$	1445.73	$B_1$	1461.06	$B_{1u}$	1467.04	$B_1$	1481.89	$A_{2u}$	1502.25
$9^l$	$4^1 3^1$	$A_{1u}$	1457.21	$A_2$	1467.30	$A_2$	1483.37	$A_u$	1490.28	$A_2$	1502.05	$A_{1u}$	1525.70
$6^u$	$4^1 5^1 + 2^1 4^1 5^1$	$E_g$	1467.38	$B_1$	1484.31	$B_1$	1497.54	$B_{2g}$	1501.83	$B_1$	1521.77	$E_g$	1535.96
$6^u$	$4^1 5^1 + 2^1 4^1 5^1$	$E_g$	1467.87	$A_2$	1489.35	$A_2$	1514.14	$B_{3g}$	1502.88	$A_2$	1524.04	$E_g$	1536.47
$9^u$	$2^1 4^1 3^1$	$B_{1u}$	1479.48	$A_2$	1506.38	$B_1$	1525.63	$A_u$	1517.84	$A_2$	1538.05	$B_{1u}$	1552.26
$10^l$	$2^2 4^5$	$B_{2u}$	1506.03	$B_1$	1525.82	$A_2$	1543.72	$B_{1u}$	1542.09	$B_1$	1561.12	$B_{2u}$	1577.91
$5^u$	$2^7 4^1 + 2^5 4^3$	$A_{2u}$	1521.18	$B_1$	1543.74	$B_1$	1566.79	$B_{1u}$	1565.99	$B_1$	1589.85	$A_{2u}$	1613.24
$11^l$	$2^2 4^1 5^1$	$E_g$	1562.59	$B_1$	1580.29	$B_1$	1593.11	$B_{2g}$	1600.07	$B_1$	1618.21	$E_g$	1639.02
$11^l$	$2^2 4^1 5^1$	$E_g$	1563.18	$A_2$	1581.59	$A_2$	1602.56	$B_{3g}$	1602.41	$A_2$	1620.06	$E_g$	1639.61

<sup>a</sup>See footnote in Table III.

complex rotational structures with different nuclear spin statistics will considerably complicate the assignments of the gas phase IR and Raman spectra at 298 K. Some of the dipole forbidden transitions are allowed in the less abundant isotopomers and will have their own weak rotational transitions. The theoretical approach developed in this work is generally applicable for tetraatomic rhombic clusters not exhibiting the Jahn–Teller effect.

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# Theoretical Study of the Electronically Excited States of $B_4$ , $B_4^+$ and $B_4^-$

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*Electronical Excitation Energies / Conical Intersections /  
Cluster UV Spectra / Electron Affinity / Ionization Energy*

First-principle full valence complete active space calculations (CASSCF) are reported for the electronic states of the  $D_{2h}$  and  $C_{2v}$  planar isomers of  $B_4$ ,  $B_4^+$  and  $B_4^-$ . This approach is found to reproduce well the experimentally known transition energies for the two lowest excited triplet states of the most stable rhombic  $B_4$  isomer. The pattern of electronic transitions up to about 4.5 eV for  $B_4$  singlet and  $B_4^+$  doublet states calculated in similar way should guide an UV spectroscopic search.

## 1. Introduction

Studies of small boron clusters are motivated by a desire to understand the manifold of chemical structures, intramolecular dynamics and reactivity of these covalently bound homonuclear molecules. There are surprisingly few reports on the spectroscopy of such neutral or charged clusters. The boron trimer was investigated in low temperature matrices by ESR [1], IR [2] and UV [3] techniques. So far only its  $2^2E' \leftarrow X^2A'_1$  electronic transition was observed in the gas phase [4]. The  $B_3$  and  $B_4$  clusters in their neutral and anionic forms were studied by photoelectron spectroscopy [5]. The first ionization energy [6–8] and the electron affinity [5] of rhombic  $B_4$  are known. The mass-spectrometric studies [9–11] on  $B_n^+$  provided information about their thermochemical stabilities and fragmentation paths.

The present contribution deals mainly with electronically excited states of  $B_4$  and  $B_4^+$ . The aim is to calculate the pattern of electronic transitions in

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rhombic and planar  $C_{2v}$  isomers to guide the spectroscopic search for these molecules. Previous theoretical works have reported the ground state equilibrium structures of various isomers, their relative stabilities, harmonic frequencies, nuclear-independent chemical shifts, dipole polarizability, hyperpolarizability, and thermochemical data [12–31]. Recently we have investigated the splittings of vibrational states in rhombic  $B_4$  [30]. So far the only theoretical study concerning the electronically excited triplet and singlet states of  $B_4$  was performed in conjunction with the assignment of the  $B_4^-$  photoelectron spectrum [5].

The boron tetramer represents a challenging problem from the point of view of electronic spectroscopy. Depending on its formation different isomers could coexist and their electronic states could lie in the same UV region. The states in rhombic isomers can correlate with electronically degenerate states of  $D_{4h}$  symmetry forming Jahn–Teller pairs. Perturbations can arise from vibronic couplings and spin multiplet crossings. As in the  $B_4$  rhombic ground state [30], the minimum/square transition state topology of the potential energy surface (PES) can lead to splittings of vibrational modes complicating the vibronic coupling effects.

The present study shows that the ground states of  $B_4^+$  and  $B_4^-$  consist of two vibronically coupled electronic states. The most intense electronic transitions in  $B_4$  and  $B_4^+$  will be those to Jahn–Teller states. It is found that the pattern of dipole allowed electronic transitions in rhombic and  $C_{2v}$  isomers should allow them to be recognized by their UV spectra.

## 2. Computational approach

All electronic structure calculations were carried out using the MOLPRO program [32]. The valence electronic configurations for the lowest isomers of the  $B_4$  electronic ground state are:

$$X^1A_g (D_{2h} \text{ rhombus}) 1a_g^2 1b_{2u}^2 1b_{3u}^2 1b_{1u}^2 1b_{1g}^2 2a_g^2$$

$$X^1A_1 (C_{2v} \text{ planar}) 1a_1^2 2a_1^2 1b_1^2 3a_1^2 1b_2^2 4a_1^2$$

$$X^1\Sigma_g^+ (D_{\infty h}) 1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 1\pi_u^4 2\sigma_u^2.$$

In the calculations of equilibrium geometries vertical and adiabatic excitation energies we used the CASSCF or state-averaged CASSCF methods [33]. In the present work the stationary points optimization was restricted to planar ( $D_{2h}$ ,  $D_{4h}$ ,  $C_{2v}$ ) or linear centro-symmetric structures. It has been known in previous calculations [12] that rhombic, planar  $C_{2v}$  and centro-symmetric structures represent local minima on the ground state PES of  $B_4$ ,  $B_4^+$  and  $B_4^-$ . For the  $B_4^+$  linear structure the symmetry of the ground state has been calculated to be  $^2\Sigma_g$  [12] and  $^2\Sigma_u$  [31], whereas the present CASSCF calculations yield a  $^2\Pi_u$  state. In the case of the  $B_4^-$  ground state a  $^2\Pi_g$  state has been

obtained [12]; we find on the other hand the lowest centro-symmetric linear isomer to have the  ${}^2\Pi_u$  symmetry. The EOM-CC method [34] was also employed for the  $B_4$  excited singlet states and some of the energy differences were calculated by the RCCSD(T) approach [35]. In most calculations the basis set used was the augmented correlation-consistent polarized valence triple zeta (aug-cc-pVTZ) [36]. The relative energies of the isomers, the ionization energy and the electron affinity were calculated by the RCCSD(T) method and the aug-cc-pVQZ basis set [36]. Our most reliable excitation energies were obtained by the full valence CASSCF method for each state of a given irreducible representation calculated separately. For singlet states the full valence active space comprised about  $1.7 \times 10^6$  CSF's for the rhombic and  $3.5 \times 10^6$  CSF's for the planar  $C_{2v}$  structures. More information about the computations is specified in the footnotes of Tables 1 to 7.

### 3. Results and discussion

The optimized  $D_{2h}$  and  $C_{2v}$  planar or centro-symmetric linear stationary points on the six-dimensional PES of the electronic ground and excited states for  $B_4$ ,  $B_4^+$  and  $B_4^-$  are given in Tables 1 to 3. The geometry parameters and symmetry axes are defined in Fig. 1. The calculated vertical and adiabatic electronic excitation energies are compiled in Tables 4 to 7. The RCCSD(T) relative energy differences between the optimized structures for the three isomers show that in all three species the most stable isomers have rhombic structures followed by planar  $C_{2v}$  structures which lie 2.18 eV ( $B_4$ ), 1.09 eV ( $B_4^+$ ), 1.55 eV ( $B_4^-$ ) (Tables 1 to 3) higher in energy, in relatively good agreement with previous theoretical findings (*cf.* Ref. [12]). The lowest dissociation energy ( $B^+({}^1S) + B_3(X\ {}^2A'_1)$ ) has been determined experimentally to be  $2.4 \pm 0.6$  eV [6], though the theoretical value was calculated several eV larger [17, 29]. The ground state PES at optimized geometries of the three isomers of  $B_4^+$  lies below this asymptotic limit. The rhombus/square energy difference of 0.031 eV on the double minimum potential of the electronic ground state of  $B_4$  leads to splittings of vibrational transitions [30]. In  $B_4^+$  ( ${}^2A_g$ ) the barrier to the square transition state is calculated to be ten times smaller and will not lead to such splittings (Table 2 and [17]). In the  ${}^2A_g$  state of  $B_4^-$  this barrier is almost three times larger (0.082 eV, Table 3) and thus the splittings will be smaller than in rhombic  $B_4$ . In the geometry region of the square saddle point of the  $B_{3u}$  state the negative ion is calculated to be unstable with respect to autoionization. The  $B_{2u}$  state correlating with the corresponding  $E_u$  state autoionizes already in the geometry region of the  $B_{3u}$  minimum.

In  $B_4^+$  the lowest  ${}^2A_g$  state lies only 0.17 eV below the  ${}^2B_{1g}$  state (Table 6, method e). Both states cross in  $D_{2h}$  structures along the ring angle coordinate (Fig. 2a), and form an avoided crossing along the  $b_{1g}$  coupling mode one (Fig. 2b). The accuracy of the *ab initio* calculated energy differences and

**Table 1.** CASSCF optimized geometries for the B<sub>4</sub> isomers and relative energy differences between their minima.

B <sub>4</sub> ( <i>D</i> <sub>2h</sub> ) rhombus					B <sub>4</sub> ( <i>D</i> <sub>4h</sub> ) square		
State	Method	<i>R</i>	<i>α</i>	<i>ΔE</i> <sub>CCSD(T)</sub> <sup><i>a</i></sup>	Method	<i>R</i>	<i>ΔE</i> <sub>CCSD(T)</sub> <sup><i>a</i></sup>
		[bohr]	[deg.]	[eV]		[bohr]	[eV]
X <sup>1</sup> A <sub>g</sub>	<i>b</i>	2.909	75.8	0	<i>b</i>	2.899	0.031
<sup>1</sup> B <sub>1u</sub>	<i>c</i>	3.134	73.9		<i>c</i>	3.266	
<sup>1</sup> B <sub>1g</sub>	<i>c</i>	3.092	61.7		<i>c</i>	3.033	
<sup>1</sup> B <sub>3u</sub>	<i>c</i>	3.007	69.8		<i>c</i>	3.007	
<sup>1</sup> B <sub>3g</sub>	<i>c</i>	3.058	60.3		<i>c</i>	2.981	
<sup>1</sup> B <sub>2g</sub>	<i>c</i>	3.060	64.7		<i>c</i>	2.981	
<sup>1</sup> B <sub>2u</sub>	<i>c</i>	3.024	59.4		<i>c</i>	3.007	
<sup>1</sup> A <sub>u</sub>	<i>c</i>	3.300	90.0		<i>c</i>	3.300	

B <sub>4</sub> ( <i>C</i> <sub>2v</sub> )					
State	Method	<i>R</i> <sub>1</sub>	<i>R</i> <sub>2</sub>	<i>θ</i>	<i>ΔE</i> <sub>CCSD(T)</sub> <sup><i>a</i></sup>
		[bohr]	[bohr]	[deg.]	[eV]
X <sup>1</sup> A <sub>1</sub>	<i>d</i>	3.227	3.026	56.8	2.182
	<i>e</i>	3.253	2.986	58.4	
<sup>1</sup> B <sub>2</sub>	<i>f</i>	3.386	3.218	54.4	
<sup>1</sup> B <sub>1</sub>	<i>f</i>	2.936	3.100	58.3	
<sup>1</sup> A <sub>2</sub>	<i>f</i>	3.207	3.205	55.2	
<sup>1</sup> A <sub>1</sub>	<i>f</i>	3.111	3.174	54.6	

B <sub>4</sub> ( <i>D</i> <sub>∞h</sub> ) linear				
State	Method	<i>R</i> <sub>1</sub>	<i>R</i> <sub>2</sub>	<i>ΔE</i> <sub>CCSD(T)</sub> <sup><i>a</i></sup>
		[bohr]	[bohr]	[eV]
X <sup>1</sup> Σ <sub>g</sub> <sup>+</sup>	<i>g</i>	2.922	2.890	2.379

<sup>*a*</sup> *ΔE*<sub>CCSD(T)</sub> relative to the X <sup>1</sup>A<sub>g</sub> state of rhombic B<sub>4</sub>; aug-cc-VQZ basis set; *E* = −98.91001460 hartree.  
*b* CCSD(T) with aug-cc-VQZ basis set.  
*c* CASSCF with aug-cc-VTZ basis set; active space: 1-3a<sub>g</sub>, 1-2b<sub>3u</sub>, 1-2b<sub>2u</sub>, 1-2b<sub>1u</sub>, 1-2b<sub>1g</sub>, 1b<sub>2g</sub>, 1b<sub>3g</sub>.  
*d* CASSCF with aug-cc-VTZ basis set; active space: 1-6a<sub>1</sub>, 1-3b<sub>1</sub>, 1-3b<sub>2</sub>.  
*e* CCSD(T) with aug-cc-VTZ basis set.  
*f* CASSCF with aug-cc-VTZ basis set; active space: 1-7a<sub>1</sub>, 1-3b<sub>1</sub>, 1-3b<sub>2</sub>, 1a<sub>2</sub>.  
*g* CASSCF with aug-cc-VTZ basis set; active space: 1-3a<sub>g</sub>, 1-3b<sub>3u</sub>, 1-2b<sub>2u</sub>, 1-2b<sub>1u</sub>, 1b<sub>1g</sub>, 1b<sub>2g</sub>.

geometries does not permit a definite answer about the mixing of both states, *i.e.* about the structure of the vibronic ground state, vibronic transitions and intensity borrowing in the UV absorption spectra.

**Table 2.** CASSCF optimized geometries for the B<sub>4</sub><sup>+</sup> isomers and relative energy differences between their minima.

B <sub>4</sub> <sup>+</sup> ( <i>D</i> <sub>2h</sub> ) rhombus					B <sub>4</sub> <sup>+</sup> ( <i>D</i> <sub>4h</sub> ) square		
State	Method	<i>R</i> [bohr]	<i>α</i> [deg.]	<i>ΔE</i> <sub>RCCSD(T)</sub> <sup><i>a</i></sup> [eV]	Method	<i>R</i> [bohr]	<i>ΔE</i> <sub>RCCSD(T)</sub> <sup><i>a</i></sup> [eV]
X <sup>2</sup> A <sub>g</sub>	<i>b</i>	2.958	79.5	0	<i>b</i>	2.913	0.003
	<i>c</i>	2.951	83.4				
<sup>2</sup> B <sub>1u</sub>	<i>d</i>	3.026	76.1		<i>d</i>	3.003	
<sup>2</sup> B <sub>1g</sub>	<i>d</i>	3.036	61.6		<i>d</i>	2.954	
<sup>2</sup> B <sub>3u</sub>	<i>d</i>	3.127	54.2		<i>d</i>	3.030	
<sup>2</sup> B <sub>2u</sub>	<i>d</i>	N.C.	N.C.		<i>d</i>	3.030	
<sup>2</sup> B <sub>3g</sub>	<i>d</i>	3.060	77.6		<i>d</i>	3.155	
<sup>2</sup> B <sub>2g</sub>	<i>d</i>	3.152	65.3		<i>d</i>	3.155	
<sup>2</sup> A <sub>u</sub>	<i>d</i>	3.247	64.4		<i>d</i>	3.159	

B <sub>4</sub> <sup>+</sup> ( <i>C</i> <sub>2v</sub> )					
State	Method	<i>R</i> <sub>1</sub> [bohr]	<i>R</i> <sub>2</sub> [bohr]	<i>θ</i> [deg.]	<i>ΔE</i> <sub>RCCSD(T)</sub> <sup><i>a</i></sup> [eV]
X <sup>2</sup> A <sub>1</sub>	<i>e</i>	3.113	3.087	56.5	1.087
	<i>c</i>	3.086	3.039	57.3	
<sup>2</sup> B <sub>2</sub>	<i>f</i>	3.602	3.149	57.1	
<sup>2</sup> B <sub>1</sub>	<i>f</i>	2.978	2.986	121.2	
<sup>2</sup> A <sub>1</sub>	<i>f</i>	3.081	3.017	61.5	
<sup>2</sup> B <sub>1</sub>	<i>f</i>	3.157	3.169	54.1	
<sup>2</sup> B <sub>2</sub>	<i>f</i>	3.187	3.196	56.7	

B <sub>4</sub> <sup>+</sup> ( <i>D</i> <sub>∞h</sub> ) linear				
State	Method	<i>R</i> <sub>1</sub> [bohr]	<i>R</i> <sub>2</sub> [bohr]	<i>ΔE</i> <sub>RCCSD(T)</sub> <sup><i>a</i></sup> [eV]
X <sup>2</sup> Π <sub>u</sub>	<i>g</i>	2.895	2.998	1.496

<sup>a</sup> *ΔE*<sub>RCCSD(T)</sub> relative to the X <sup>2</sup>A<sub>g</sub> state of rhombic B<sub>4</sub><sup>+</sup>; aug-cc-VQZ basis set; *E* = −98.54990461 hartree.  
*b* CASSCF with aug-cc-VTZ basis set; active space: 1-3a<sub>g</sub>, 1-2b<sub>3u</sub>, 1-2b<sub>2u</sub>, 1-2b<sub>1g</sub>, 1-2b<sub>1u</sub>.  
*c* RCCSD(T) with aug-cc-VTZ basis set.  
*d* CASSCF with aug-cc-VTZ basis set; active space: 1-3a<sub>g</sub>, 1-2b<sub>3u</sub>, 1-2b<sub>2u</sub>, 1-2b<sub>1u</sub>, 1-2b<sub>1g</sub>, 1b<sub>2g</sub>, 1b<sub>3g</sub>; the optimization for the <sup>2</sup>B<sub>2u</sub> state did not converge.  
*e* CASSCF with aug-cc-VTZ basis set; active space: 1-7a<sub>1</sub>, 1-2b<sub>1</sub>, 1-3b<sub>2</sub>.  
*f* CASSCF with aug-cc-VTZ basis set; active space: 1-7a<sub>1</sub>, 1-3b<sub>1</sub>, 1-3b<sub>2</sub>, 1a<sub>2</sub>.  
*g* CASSCF with aug-cc-VTZ basis set; active space: 1-3a<sub>g</sub>, 1-3b<sub>3u</sub>, 1-2b<sub>2u</sub>, 1-2b<sub>1u</sub>, 1b<sub>1g</sub>, 1b<sub>2g</sub>.

**Table 3.** CASSCF optimized geometries for the  $B_4^-$  isomers and relative energy differences between their minima.

$B_4^- (D_{2h})$ rhombus					$B_4^- (D_{4h})$ square		
State	Method	$R$ [bohr]	$\alpha$ [deg.]	$\Delta E_{\text{RCCSD(T)}}^a$ [eV]	Method	$R$ [bohr]	$\Delta E_{\text{RCCSD(T)}}^a$ [eV]
$X \ ^2B_{3u}$	<i>b</i>	2.992	63.3	0	<i>b</i>	2.922	
$\ ^2A_g$	<i>c</i>	3.035	68.6	0.050	<i>c</i>	3.007	0.082

$B_4^- (C_{2v})$					
State	Method	$R_1$ [bohr]	$R_2$ [bohr]	$\theta$ [deg.]	$\Delta E_{\text{RCCSD(T)}}^a$ [eV]
$X \ ^2A_1$	<i>d</i>	3.226	3.050	56.8	1.546
$\ ^2B_1$	<i>e</i>	3.097	3.069	60.9	2.014

$B_4^- (D_{\infty h})$ linear				
State	Method	$R_1$ [bohr]	$R_2$ [bohr]	$\Delta E_{\text{RCCSD(T)}}^a$ [eV]
$X \ ^2\Pi_u$	<i>f</i>	2.919	3.103	2.866

<sup>a</sup>  $\Delta E_{\text{RCCSD(T)}}$  relative to the  $X \ ^2B_{3u}$  state of rhombic  $B_4^-$ ; aug-cc-VQZ basis set;  $E = -98.96948401$  hartree.

*b* CASSCF with aug-cc-VTZ basis set; active space: 1-3a<sub>g</sub>, 1-3b<sub>3u</sub>, 1-2b<sub>2u</sub>, 1-2b<sub>1g</sub>, 1-2b<sub>1u</sub>.

*c* CASSCF with aug-cc-VTZ basis set; active space: 1-4a<sub>g</sub>, 1-2b<sub>3u</sub>, 1-2b<sub>2u</sub>, 1-2b<sub>1g</sub>, 1-2b<sub>1u</sub>.

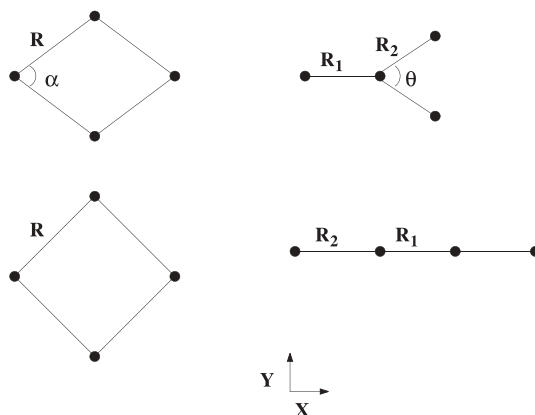
*d* CASSCF with aug-cc-VTZ basis set; active space: 1-7a<sub>1</sub>, 1-4b<sub>1</sub>, 1b<sub>2</sub>.

*e* CASSCF with aug-cc-VTZ basis set; active space: 1-6a<sub>1</sub>, 1-4 b<sub>1</sub>, 1-3b<sub>2</sub>.

*f* CASSCF with aug-cc-VTZ basis set; active space: 1-4a<sub>g</sub>, 1-3b<sub>3u</sub>, 1-2b<sub>2u</sub>, 1-2b<sub>1u</sub>, 1b<sub>1g</sub>, 1b<sub>2g</sub>.

Similar coupling is found also for the ground state of  $B_4^-$ . In the adiabatic picture the  $\ ^2B_{3u}$  state is calculated only 0.05 eV below the  $\ ^2A_g$  state (Table 3, and Ref. [5]). Also in this case both states cross in  $D_{2h}$  structures along the ring angle coordinate (Fig. 3a), and form an avoided crossing along the b<sub>3u</sub> coupling mode (Fig. 3b).

The adiabatic aug-cc-pVQZ/RCCSD(T) ionization energy  $IE_e$  of  $B_4$  has been calculated to be 9.799 eV for the rhombic, 8.705 eV for the planar  $C_{2v}$  and 8.916 eV for the linear structures using the optimized geometries (Tables 1 to 2). The first is in excellent agreement with the experimental value of 9.8 eV [2–4]. Similar approach yields adiabatic electron affinities of 1.618 eV (negative ion in  $\ ^2B_{3u}$  state) and 1.568 eV (in  $\ ^2A_g$  state) for the rhombic isomer, 1.786 eV (in  $\ ^2B_1$  state) and 2.254 eV (in  $\ ^2A_1$ ) for the  $C_{2v}$  isomer, and 1.131 eV (in  $\ ^2\Pi_u$  state) for the linear  $B_4^-$  (*cf.* also Ref. [12]). The two higher isomers



**Fig. 1.** Definition of the coordinates and symmetry axis in  $B_4$  isomers.

have well defined electronic wavefunctions indicating that spontaneous electron detachment does not take place. The planar  $C_{2v}$  isomer ( $^2A_1$ ) is calculated to lie just below the autodetachment threshold of 1.6 eV [5] (Table 3). The electronically excited states will autoionize, but the ground state six-dimensional PES has large portions on which the additional electron is bound, particularly along the isomerization paths.

The full valence CASSCF calculations of vertical excitation energies confirm that the ionization of  $B_4^-$  leads to triplet states of  $B_4$  (Table 4). Our results agree well with the RCCSD(T) values [5], and with the positions of the first two observed bands in the photoelectron spectrum. This good agreement with experiment allows us to assume that other excitation energies calculated with this approach will be of similar accuracy.

The vibronic coupling in  $B_4^-$  ground state mixes gerade and ungerade wavefunctions. In its photoelectron spectrum only the ionizations to ungerade triplet states were assigned. In Table 4 we compare the vertical excitation energies relative to the singlet ground state of  $B_4$  but calculated for the optimized geometries of the  $^2B_{3u}$  and  $^2A_g$  states of  $B_4^-$ . Whereas the energy differences for the first two triplet states agree nicely with experiment for the geometry of the  $^2B_{3u}$  state, they disagree for the second structure. This supports the assumption made in [5] that the lowest part of the PES for the ground state of the negative ion is dominated by the  $^2B_{3u}$  wavefunction. The lowest triplet states  $^3B_{2u}$  and  $^3B_{3u}$  correlate with the  $^3E_u$  state in  $D_{4h}$  symmetry; the observed band corresponds to a Jahn–Teller system. The experimental spectrum at higher energies is more difficult to assign because several triplets and singlets are calculated to lie close to the observed band at about 2.4 eV (Table 4).

In Table 5 the vertical and adiabatic transition energies in rhombic and square geometries for the singlet states of  $B_4$  are compared. Only one elec-

**Table 4.** Comparison of the experimental and calculated energy differences in B<sub>4</sub> at the optimized geometries of the <sup>2</sup>B<sub>3u</sub> and <sup>2</sup>A<sub>g</sub> states of rhombic B<sub>4</sub><sup>−</sup>.

	$T_v^a$ [eV]	$T_v^b$ [eV]	$T_v^c$ [eV]	Experiment [eV]
X <sup>1</sup> A <sub>g</sub>	0	0	0	0
a <sup>3</sup> B <sub>2u</sub>	1.29	2.18	1.29	1.09
b <sup>3</sup> B <sub>3u</sub>	1.43	1.95	1.39	1.42
c <sup>3</sup> B <sub>1g</sub>	1.64	1.84	1.74 <sup>d</sup>	
A <sup>1</sup> B <sub>1g</sub>	2.03			
B <sup>1</sup> B <sub>2u</sub>	2.13			
d <sup>3</sup> A <sub>g</sub>	2.55	1.75	1.60 <sup>d</sup>	
e <sup>3</sup> B <sub>2g</sub>	2.60	2.80	2.50	
C <sup>1</sup> B <sub>2g</sub>	2.84			
f <sup>3</sup> B <sub>1u</sub>	2.85	2.37	2.18 <sup>d</sup>	2.40
D <sup>1</sup> B <sub>1u</sub>	3.36			

<sup>a</sup> Full-valence CASSCF; aug-cc-pVTZ basis set; each state calculated separately at the optimized geometry of the X <sup>2</sup>B<sub>3u</sub> state of B<sub>4</sub><sup>−</sup>: *R* = 3.015 bohr, *α* = 63.6 degrees [5]; *E* = −98.69773452 hartree.

<sup>b</sup> Full-valence CASSCF; aug-cc-pVTZ basis set; each state calculated separately at the optimized geometry of the X <sup>2</sup>A<sub>g</sub> state of B<sub>4</sub><sup>−</sup>: *R* = 3.064 bohr, *α* = 73.8 degrees [5]; *E* = −98.69847200 hartree.

<sup>c</sup> RCCSD(T); each state calculated at the optimized geometry of the X <sup>2</sup>B<sub>3u</sub> state of B<sub>4</sub><sup>−</sup>: *R* = 3.015 bohr, *α* = 63.6 degrees [5].

<sup>d</sup> RCCSD(T); each state calculated at the optimized geometry of the X <sup>2</sup>A<sub>g</sub> state of B<sub>4</sub><sup>−</sup>: *R* = 3.064 bohr, *α* = 73.8 degrees [5].

**Table 5.** Vertical (*T<sub>v</sub>*) and adiabatic (*T<sub>e</sub>*) excitation energies and transition moments (*μ<sub>e</sub>*) between singlet states of rhombic and square B<sub>4</sub>.

	Rhombus					Square				
	$T_{v,av}^a$ [eV]	$\mu_e$ [debye]	$T_{v,EOM}^b$ [eV]	$T_v^c$ [eV]	$T_e^d$ [eV]	$T_{v,av}^a$ [eV]	$\mu_e$ [debye]	$T_{v,EOM}^b$ [eV]	$T_v^c$ [eV]	$T_e^d$ [eV]
X <sup>1</sup> A <sub>g</sub>	0		0	0	0	0		0	0	0
A <sup>1</sup> B <sub>1g</sub>	2.91		3.12	2.94	2.12	2.98		3.35	3.10	2.87
B <sup>1</sup> B <sub>2u</sub>	3.44	0.6889 (y)	3.71	3.52	2.20	4.57	1.6642 (y)	4.63	4.56	4.19
C <sup>1</sup> B <sub>1u</sub>	3.56	0.2412 (z)	3.49	3.61	2.89	3.40	0.0000 (z)	3.43	3.46	3.30
D <sup>1</sup> B <sub>2g</sub>	3.74		3.74	3.77	2.94	5.19		4.48	5.30	4.68
E <sup>1</sup> B <sub>3u</sub>	3.99	2.3070 (x)	3.85	4.12	3.82	4.57	1.6642 (x)	4.63	4.56	4.19
F <sup>1</sup> B <sub>3g</sub>	4.66		4.55	4.58	3.90	5.19		4.48	5.30	4.68

<sup>a</sup> Full-valence SA-CASSCF with aug-cc-pVTZ basis set at the optimized geometry of X <sup>1</sup>A<sub>g</sub> (Table 1); one state per irreducible representation calculated.

<sup>b</sup> At the optimized geometry of X <sup>1</sup>A<sub>g</sub> (Table 1); aug-cc-pVQZ basis set.

<sup>c</sup> Full-valence CASSCF with aug-cc-pVTZ basis set at the optimized geometry of X <sup>1</sup>A<sub>g</sub> (Table 1); each state calculated separately.

<sup>d</sup> Full-valence CASSCF with aug-cc-pVTZ basis set at optimized geometry (Table 1); each state calculated separately.

**Table 6.** Vertical ( $T_v$ ) and adiabatic ( $T_e$ ) excitation energies and transition moments ( $\mu_e$ ) between doublet and quartet states of rhombic and square B<sub>4</sub><sup>+</sup>.

	Rhombus				Square			
	$T_{v,av}^a$ [eV]	$\mu_e^b$ [debye]	$T_v^c$ [eV]	$T_e^d$ [eV]	$T_{v,av}^a$ [eV]	$\mu_e^b$ [debye]	$T_v^c$ [eV]	$T_e^d$ [eV]
X <sup>2</sup> A <sub>g</sub>	0		0					
A <sup>2</sup> B <sub>1g</sub>	0.58		0.70	0.17	0.73		0.78	0.74
B <sup>2</sup> B <sub>1u</sub>	0.63	0.9796 (z)	0.70	0.62	0.68	1.0374 (z)	0.75	0.60
a <sup>4</sup> B <sub>1g</sub>	1.99				2.13			
b <sup>4</sup> B <sub>1u</sub>	2.35				2.35			
C <sup>2</sup> A <sub>g</sub>	2.50							
c <sup>4</sup> B <sub>2u</sub>	2.72	1.4404 (x)			3.94	1.1402 (x)		
D <sup>2</sup> B <sub>1u</sub>	2.93	0.2431 (z)						
E <sup>2</sup> B <sub>1g</sub>	2.94							
F <sup>2</sup> B <sub>3u</sub>	3.03	1.7305 (x)	3.04	1.64	3.69	0.7120 (x)	3.52	3.35
G <sup>2</sup> B <sub>2u</sub>	3.17	1.3820 (y)			3.69	0.7120 (y)	3.52	3.35
d <sup>4</sup> B <sub>2g</sub>	3.21				4.39			
e <sup>4</sup> A <sub>u</sub>	3.28	0.8564 (z)			3.74	0.9007 (z)		
H <sup>2</sup> B <sub>2g</sub>	3.63		3.71	2.46	4.96		4.79	3.75
f <sup>4</sup> B <sub>3g</sub>	3.75				4.39			
I <sup>2</sup> B <sub>2u</sub>	3.81	0.6198 (y)						
J <sup>2</sup> A <sub>u</sub>	4.07		4.15	2.93	4.68		4.44	3.48
g <sup>4</sup> B <sub>3u</sub>	4.13	0.1174 (y)			3.94	1.1402 (y)		
K <sup>2</sup> A <sub>u</sub>	4.17							
L <sup>2</sup> B <sub>3u</sub>	4.28	0.8819 (x)						
M <sup>2</sup> B <sub>3g</sub>	4.31		4.44	3.86	4.96		4.79	3.75

<sup>a</sup> Full-valence SA-CASSCF with aug-cc-pVTZ basis set at the optimized geometry of X <sup>2</sup>A<sub>g</sub> (Table 2); two states per irreducible representation calculated.  
<sup>b</sup> For the quartet states the transition moments are given with respect to the lowest <sup>4</sup>B<sub>1g</sub>.  
<sup>c</sup> Full-valence CASSCF with aug-cc-pVTZ at the optimized geometry of X <sup>2</sup>A<sub>g</sub> (Table 2); each state calculated separately.  
<sup>d</sup> Full-valence CASSCF with aug-cc-pVTZ basis set at optimized geometry (Table 2); each state calculated separately.

tronic state in a given irreducible representation has been considered. The state averaged calculations needed for the transition moments yield transition energies which deviate from those calculated for each state separately by less than about 0.1 eV. The CC-EOM vertical transition energies differ from the full valence CASSCF results by up to 0.2 eV. The absorption spectrum of B<sub>4</sub> will have strong bands (*cf.* transition moments in Table 5) to the <sup>1</sup>B<sub>2u</sub> state starting around 2.20 eV and the <sup>1</sup>B<sub>3u</sub> state around 3.82 eV. These states form a Jahn–Teller pair, the D<sub>4h</sub> E<sub>u</sub> structure is calculated to lie 2 eV and 1.45 eV above the equilibrium energies of the two rhombic components. Though the transitions to the Jahn–Teller pair in gerade symmetry are symmetry forbidden, they could gain intensity by

**Table 7.** Vertical ( $T_v$ ) and adiabatic ( $T_e$ ) excitation energies and transition moments ( $\mu_e$ ) between singlet states of  $C_{2v}$   $B_4$  and between doublet states of  $C_{2v}$   $B_4^+$ .

	$B_4$					$B_4^+$			
	$T_{v,av}^a$ [eV]	$\mu_e$ [debye]	$T_v^b$ [eV]	$T_e^c$ [eV]		$T_{v,av}^a$ [eV]	$\mu_e$ [debye]	$T_v^b$ [eV]	$T_e^c$ [eV]
X $^1A_1$	0		0	0	X $^2A_1$	0			
A $^1A_1$	1.27	1.6832 (x)	1.35	0.41	A $^2B_2$	1.33	0.3485 (z)	1.37	1.15
B $^1B_1$	1.90	0.9179 (y)	1.76	1.50	B $^2A_1$	1.47	0.2443 (x)	1.52	1.32
C $^1B_2$	2.37	0.2348 (z)	2.21	2.01	C $^2B_1$	1.71	0.4057 (y)	1.76	1.06
D $^1B_2$	2.43	1.2223 (z)	N.C.		D $^2A_2$	1.94			
E $^1A_2$	2.50		2.53	2.35	E $^2B_2$	2.04	0.6730 (z)	2.03	1.93
F $^1B_1$	2.58	0.3910 (y)	2.61		F $^2B_1$	2.51	0.5600 (y)	2.58	2.51
G $^1A_2$	3.10		3.75		G $^2A_2$	2.73			

<sup>a</sup> Full-valence SA-CASSCF with aug-cc-pVTZ basis set at the optimized geometry of X  $^1A_1$  (Table 3); two states per irreducible representation calculated.

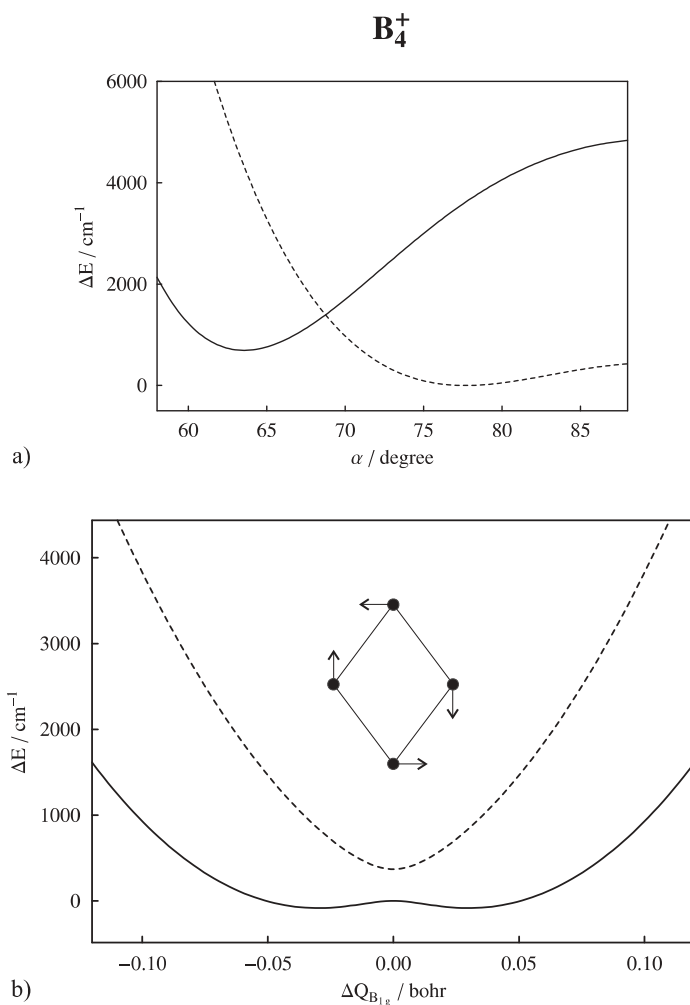
<sup>b</sup> Full-valence CASSCF with aug-cc-pVTZ basis set at the optimized geometry of X  $^1A_1$  (Table 3); each state calculated separately.

<sup>c</sup> Full-valence CASSCF with aug-cc-pVTZ basis set at optimized geometry (Table 3); each state calculated separately.

vibronic coupling via the  $b_{3u}$  mode with the close lying ungerade states (Table 5).

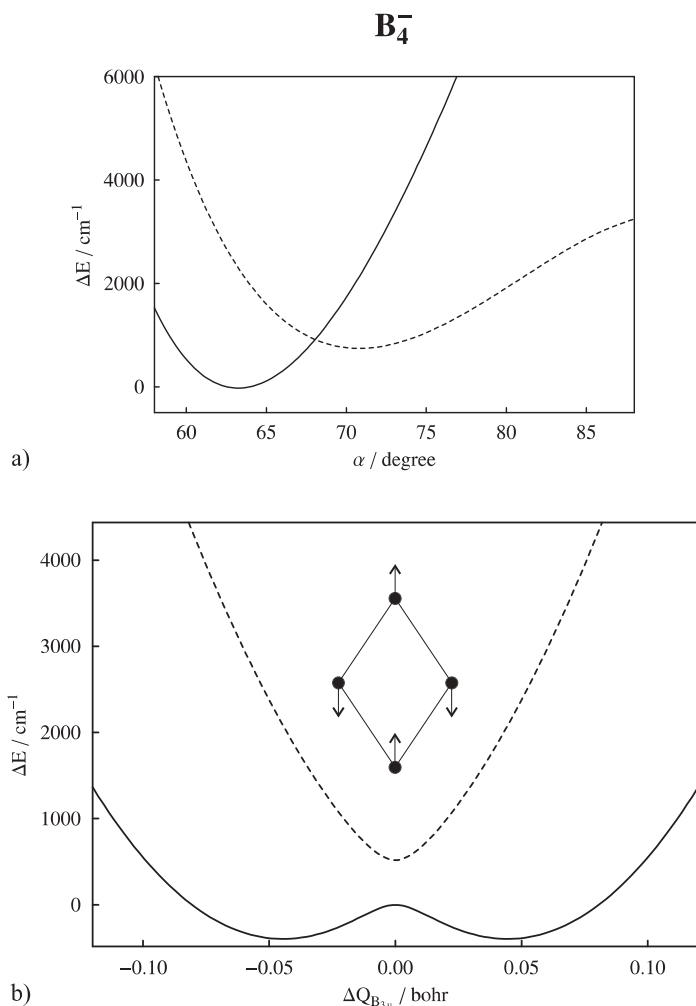
In  $B_4^+$  two excited doublet states lie lower than the first quartet state (Table 6). As discussed, the  $^2B_{1g}$  state is calculated only 0.17 eV above X  $^2A_g$  and both are vibronically coupled. Due to possible intensity borrowing it is difficult to calculate reliable radiative transition probabilities for the absorption spectra. Nevertheless in the doublet states the most intense transitions should again be those to the Jahn–Teller states  $^2B_{3u}$  and  $^2B_{2u}$  for which the vertical energy difference is calculated to be about 3.1 eV. The computations of the stationary point in  $D_{2h}$  symmetry for the second  $^2B_{2u}$  component (Table 2) did not converge because of the perturbation by other electronic states. Also the vertical energy differences for the quartet states are given in Table VI. The transition moments between these states are given relative to the lowest  $^4B_{1g}$  state.

The  $C_{2v}$  minima are calculated higher than those of the rhombic isomers (Tables 1 and 2). In Table 7 the vertical and adiabatic excitation energies for these isomers are given. Providing that both rhombic and  $C_{2v}$  isomers co-exist in the sample, the UV spectra will show transitions for both species. In  $B_4$  the most intense transitions are calculated to the  $^1A_1$ ,  $^1B_1$  and  $^1B_2$  states (Table 7), which lie much lower than the first allowed singlet transition in the rhombic isomer. This pattern should allow the isomers to be distinguished from their electronic spectra. In the case of  $B_4^+$  the comparison of energy differences in Tables 6 and 7 shows that the pattern of electronic tran-



**Fig. 2.** One dimensional cut in  $D_{2h}$  symmetry along the ring angle coordinate and  $R_e = 2.958$  bohr (cf. Table 2) of the  ${}^2A_g$  and  ${}^2B_{1g}$  states of  $B_4^+$ . Lower (broken line) and upper (full line) potentials correspond to the  ${}^2A_g$  and  ${}^2B_{1g}$  states respectively. In the SA-CASSCF calculations (cc-pVTZ, active space 3-5a<sub>g</sub>, 2-3b<sub>3u</sub>, 2-3b<sub>2u</sub>, 1b<sub>1g</sub>, 1-2b<sub>1u</sub>, 1b<sub>2g</sub>, 1b<sub>3g</sub>) both states were averaged with equal weights. In lower part of the figure the avoided crossing along the  $B_{1g}$  coupling mode for  $R_e^{\text{ref}} = 2.958$  bohr and apex angle of  $\alpha^{\text{ref}} = 68$  degrees is shown.

sitions will make such an identification more difficult, though also in this case bands below about 1.5 eV will advocate the presence of the second isomer.



**Fig. 3.** One dimensional cut in  $D_{2h}$  symmetry along the ring angle coordinate and  $R_e = 2.992$  bohr (cf. Table 2) of the  $^2A_g$  and  $^2B_{3u}$  states of  $B_4^-$ . Lower (full line) and upper (broken line) potentials correspond to the  $^2B_{3u}$  and  $^2A_g$  states respectively. In the SA-CASSCF calculations (cc-pVTZ, active space 3-6a<sub>g</sub>, 2-3b<sub>3u</sub>, 2-3b<sub>2u</sub>, 1b<sub>1g</sub>, 1b<sub>1u</sub>, 1b<sub>2g</sub>, 1b<sub>3g</sub>) both states were averaged with equal weights. In lower part of the figure the avoided crossing along the  $B_{3u}$  coupling mode for  $R_e^{\text{ref}} = 2.992$  bohr and apex angle of  $\alpha^{\text{ref}} = 67$  degrees is shown.

## 4. Summary and conclusions

So far only the photodetachment spectrum of rhombic  $B_4^-$  [5] has provided experimental information on the singlet ground and excited triplet states of  $B_4$  for

a comparison with theoretical results. The calculated full valence CASSCF excitation energies for the observed two lowest triplet states agree to within about 0.1 eV with the experimental band positions. A similar computational approach was employed to calculate vertical and adiabatic excitation energies up to about 4.5 eV for  $B_4$  and  $B_4^+$ , including the electronic transition moments, which could aid the search for boron tetramers by electronic spectroscopy. In the rhombic ground state of the charged clusters the Born–Oppenheimer approximation fails; in  $B_4^+$  the  $^2A_g$  and  $^2B_{1g}$  states are coupled by the  $b_{1g}$  vibration, in  $B_4^-$  the  $^2A_g$  and  $^2B_{3u}$  states by the  $b_{3u}$  mode.

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